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THE EFFECTS OF FREEZING ON AQUEOUS AVAILABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS FROM A CREOSOTE CONTAMINATED SOIL

BY

ANGELA ANNE THERESE BEVEL ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE**

IN

ENVIRONMENTAL ENGINEERING

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

FALL, 1995

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UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled **The Effects of Freezing on Aqueous Availability of Polycyclic Aromatic Hydrocarbons from a Creosote Contaminated Site** submitted by **Angela Anne Therese Bevel** in partial fulfillment of the requirements for the degree of **Master of Science** in **Environmental Engineering**.

Dr. S. E. Hrudey

Marvin J. Dudas

Dr. M. J. Dudas

Dr. D. C. Sego

Dr. S. J. Stanley

September 22, 1995

Abstract

A variety of methods have been tested in attempts to remediate contaminated sites. Fine-grained soils are particularly problematic to remediate because fine soil particles have a high affinity for soil contaminants, and the very small soil micropores which effectively trap contaminants.

Freezing of soil causes particle restructuring and reorganization, with different pore structures and soil grain arrangements found after freezing. Some factors affecting restructuring include soil moisture content, freezing rate, freezing end-point temperature, and number of freezing cycles.

This thesis presents experiments which determined if freezing creosote contaminated soil changes accessibility of 16 priority PAHs to the aqueous phase, through measurement of aqueous phase contaminant dissolution before and after freezing under controlled laboratory conditions. Aqueous dissolution was selected since water is the primary solvent in naturally occurring systems, and water represents a limiting scenario since many of the PAHs have low aqueous solubilities. The experiment was designed to test the effect of varying soil moisture content, freezing rate, and the location of the soil sampling following freezing to determine if the PAHs migrate through the soil. A highly contaminated sandy soil and a low-level contaminated clay soil were tested.

The results of hypothesis testing show that freezing is not a significant variable for the sand soil. Freezing was significant at 5% and 10% significance levels for a few PAHs with the clay soil.

Freezing did not demonstrate a significant effect on the migration of PAHs within the soil. However, the method of detection was through the aqueous phase only which may have prohibited adequate detection of PAH migration. Also, more sampling locations should have been tested to adequately determine if migrations of PAHs was occurring.

Soil moisture content was not a significant variable for the sand. Soil moisture content was significant at the 1% level for several of the PAHs analyzed in the clay soil. This agrees with expected results for the clay.

Freezing rate was not a significant variable for either soil tested. However, the variation of freezing rate was significantly limited by the equipment used for the experiment. The slow and fast rate varied by only 25%, which may not have been enough of a difference in freezing rate to have a detectable effect on the aqueous phase concentrations.

Many of the data sets for the heavier PAHs (heavier than pyrene) were unusable due to high coefficients of variation in the analytical results. Only data sets with coefficients of variation ranging from 5% to 30% were analyzed statistically. The variability could be due to the non-homogeneous nature of contaminated soil, laboratory errors, contaminated glassware (PAHs adsorbed to it), and the GC/MS not being adequately cleaned before use for the experimental runs for this thesis. However, the aqueous phase PAH concentrations obtained in this research represent values from a "real" soil, obtained in the field, and unaltered in the laboratory. High coefficients of variation are expected for field-obtained soil samples.

Water was confirmed as a very poor solvent for the 16 Priority PAHs tested. Many of the data sets were unusable because the aqueous phase concentrations were not consistent. This is particularly true for the lower solubility PAHs with molecular masses greater than benz(a)anthracene. Also, calculations found that only approximately 0.3% and 4.0% of the PAHs present in the oil phase partitioned into the aqueous phase for the sand and clay respectively. This represents a very small fraction of the total PAHs present.

Acknowledgments

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List of Abbreviations
(in order of appearance)

PAH- Polycyclic aromatic hydrocarbon
CCME- Canadian Council of Ministers of the Environment
PCBs- Polychlorinated biphenyls
K_{ow} - Octanol-water partition coefficient (octanol represents an organic medium)
DNAPL- Dense (more dense than water) non-aqueous phase (low solubility) liquid
LNAPL- Light (less dense than water)non-aqueous phase liquid
U.S. Army CRREL- U.S. Army Cold Regions Research and Engineering Laboratory
VOC- Volatile organic carbon
ANOVA- Analysis of variance (statistical technique)
TPHC- Total petroleum hydrocarbon contamination
ASTM- American Society for Testing and Materials
G_s- Specific gravity
RTDs- Resistance temperature devices
GC- Gas chromatograph
MSD- Mass selective detector
SIM- Selected ion monitoring
GC/MS- Gas chromatography/mass spectrometry
SPE- Solid phase extraction
C.V.- Coefficient of variation
DCM- Dichloromethane
R.F.- Response factor

1.0. INTRODUCTION

1.1. Problem Statement

A recent significant issue in North America is the treatment and management of contaminated soils. In the U.S. alone, as many as 5400 toxic waste sites at Federal Government facilities have been identified as requiring clean-up. The estimated total cost is in the order of one hundred billion dollars (Ayorinde *et al.*, 1988). In terms of human health risks, contaminated land is now widely recognized as a potential threat to environmental health (CCME, 1991).

There are many different types of contaminants found in soils, including PCBs, hydrocarbons, mercury, and trichloroethylene. Each contaminant has its own unique characteristics, and its own toxic risk to humans based on the dose delivered. Risk assessments for humans for a specific site are based on factors such as compound toxicity, bioavailability to humans via inhalation, dermal contact, and ingestion (Pollard *et al.*, 1993)

Chemicals used for certain applications have been identified as posing a potential health hazard to humans. One major application is the wood preserving industry, which currently uses more pesticides than any other industry on a volume basis. The major pesticides in use are creosote, pentachlorophenol, and a copper-chrome-and arsenate mixture. Creosote was widely used as a wood preservative in the past. It is estimated that in the U.S. alone, wood preserving operations use approximately $4.5x10^7$ kilograms (45,000,000 kg) of creosote annually (Mueller *et al.*, 1989).

Creosote is an oily substance made up of over 200 compounds. One class of compounds in creosote is the polycyclic aromatic hydrocarbons (PAHs), many of which are carcinogenic in rodent testing at relatively low levels (Fawell and Hunt, 1988). As well, epidemiological studies of some occupation-associated skin cancers in humans provide strong evidence of the role of PAHs in certain kinds of human cancers (Fawell and Hunt, 1988). Within creosote, PAHs can represent a fraction of 50-90% of the material by weight (Priddle and MacQuarrie, 1994).

Because of their hazard and potential risk for humans, PAH contaminated sites cannot be ignored and often require clean-up or other risk management measures. Current site remediation technologies may be broadly grouped into the categories of containment/immobilization, mobilization, and destruction techniques (Hrudey and Pollard, 1993). In terms of destruction, which is the only option which seeks to significantly lower concentration levels of the contaminant, bioremediation or the use of microorganisms to degrade certain compounds has shown the most promise and general applicability (Mueller *et al.*, 1989). For bioremediation to be feasible however, certain requirements and constraints in the soil must be met. One of these requirements is that the contaminant be bioavailable. For this thesis, the term bioavailable will refer to the availability of a substrate to the microbes that are capable of destroying it (Hrudey and Pollard, 1993).

One potential means of improving the bioavailability, or accessibility of the PAHs in creosote, is through ground freezing. The effect of ground freezing in altering the structure of soils is well documented (Baver, 1956; Benoit and Voorhees, 1990; Chamberlain and Blouin, 1977; Coutard and Moucher, 1985). This structural reorganization of soils may open dead end pores and rearrange soil grains, thus potentially improving accessibility to the contaminant in pore water which will subsequently enhance accessibility for microbial degradation.

1.2. Research Objectives and Scope of Project

Based on the above discussion, the overall objective of this thesis was to determine if freezing and thawing a soil increases the availability of PAH contamination to the aqueous phase in which microbes may degrade these hydrocarbons. Additional subobjectives included:

(1) Determining which factors, if any, coupled with freezing enhance the release of PAHs to the aqueous phase;

(2) If any factors were found significant, determining the relationship between these factors and aqueous availability so that any increase in aqueous availability caused by freezing may be optimized.

1.3. Thesis Organization

The thesis is organized as follows:

- Chapter 1 provides an introduction to the thesis subject, as well as the basic research objectives.
- Chapter 2 provides an overview of related research and develops the hypotheses to be tested in the experimental section of this thesis.
- Chapter 3 outlines the methods used to test the hypotheses as well as the rationale for those methods.
- Chapter 4 provides the primary data results, as well as an overview of statistical data screening and statistical procedures used to determine significance of variables.
- Chapter 5 provides the final results from the statistical analysis of the data and a discussion of the findings.
- Chapter 6 provides the final conclusions.
- Chapter 7 provides direction for possible related research and suggestions for improvement on the research performed.

2.0. EXPERIMENT RATIONALE AND THEORY

2.1. Problem Identification

In 1989, there were over 400 creosoting operations existing in the U.S. alone, and hundreds more have since been dismantled and ceased operation. The major chemicals in use by these facilities included creosote, pentachlorophenol, and a chromium-copper-arsenate mixture (Mueller *et al.*, 1989). Several abandoned wood preserving sites have been identified in Alberta, and have been identified as potentially posing a risk to human health and the environment (Pollard *et. at.*, 1993). Indeed, contaminated wood preserving sites across Canada have been cause for recent concern (CCME, 1991). Concern regarding these sites lies with the components of the contaminants at the sites. The contaminants frequently include many of the aromatic hydrocarbons such as benzene and toluene, polychlorinated phenols, lower chlorophenols and associated polychlorinated dioxins and furans, and the polycyclic aromatic hydrocarbons (PAHs) (Pollard *et al.*, 1993). The aromatic hydrocarbons were used or generated by some industries in substantial quantities (Fawell and Hunt, 1988).

The health effect associated with some PAHs which raises the greatest concern is carcinogenicity. Malignant tumors can be induced in animals by very small exposure doses of certain PAHs, such as benzo(a)pyrene, and with very short latency periods (Fawell and Hunt, 1988). In long term studies on mice, rats, guinea pigs, and rabbits, it has been demonstrated that the carcinogenic activity of base oils, greases, and waxes is due to the PAH fraction. The most potentially carcinogenic substances have been found among the 4,5,and 6 condensed ring PAH compounds with relative molecular masses ranging from 230-330 (WHO, 1982). Because chemicals found to be carcinogens in animals are generally regarded as probable carcinogens for humans, PAHs must be approached with caution since some of them are documented experimental carcinogens in animals. The metabolism and DNA binding products of one PAH, benzo(a)pyrene, in human cells and tissues are similar to those seen in susceptible experimental animals (Dipple, 1985). Human evidence of carcinogencity caused by PAHs includes reports indicating higher incidences of respiratory tract and upper gastrointestinal tract tumors associated with occupational exposures to PAHs (Dipple, 1985). Epidemiological studies of some occupation-associated skin cancers in humans provide strong evidence of the role of PAHs in certain kinds of human cancers (Fawell and Hunt, 1985). Indeed, the U.S. Environmental Protection Agency (U.S. EPA) has placed 16 of the PAH compounds on their Priority Pollutant List, which means the compounds have been targeted as being particularly hazardous to human health and require careful monitoring (Nowicki *et al.*, 1980, and Birnstingl *et al.*, 1990). These sixteen compounds and their corresponding ring structures are shown in Figure 2.1.

In summary, creosote contaminated sites may pose a health risk to humans and other biota. As a result of this potential risk, creosote contaminated sites require investigation and management to minimize the risk to biota from the site.

2.2. Remediation Technology

Current remediation technologies may be broadly grouped into the categories of containment and immobilization, mobilization, and destruction. Destruction is the only alternative that eliminates the compounds of concern (Hrudey and Pollard, 1993).

In terms of elimination technology, there are several different means. For hydrocarbon contaminated soils, bioremediation is finding increasing application (Pollard *et al.*, 1993; Ellis *et al.*, 1991; Hrudey and Pollard, 1993). Bioremediation does not come without limitations, however. In order for bioremediation to be an effective elimination treatment, several requirements must be fulfilled for biodegradation to occur. These include the contaminating material must be amenable to biological degradation, and the necessary chemistry for degradation to occur must exist. If the contaminant chemical structure is such that it is recalcitrant to degradation, bioremediation is not possible. Biological requirements must also be met, in that the soil must contain microorganisms which are capable of degrading the compound of interest. Another consideration is that degradation produces intermediate products which must also be degradable. A situation may conceivably be made worse through bioremediation if the intermediate products are more difficult to degrade and are more hazardous than the parent compounds (Hrudey

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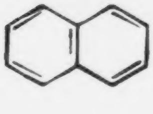

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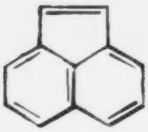

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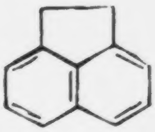

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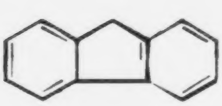

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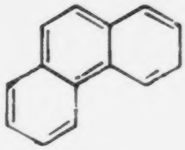

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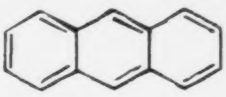

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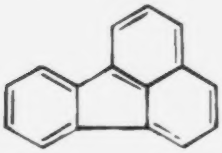
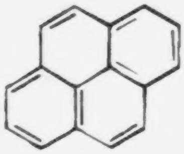
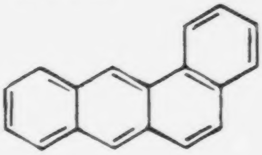


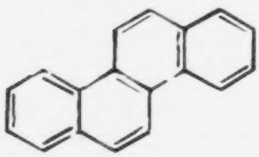
PYRENE
A.M.=202



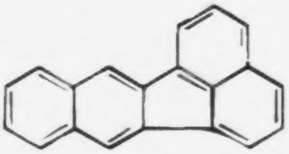
BENZ(a)ANTHRACENE
A.M.=228



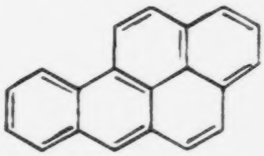
CHRYSENE
A.M.=228



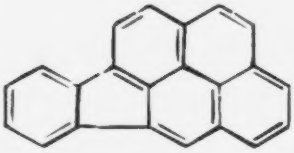
BENZO(k)FLUORANTHENE
A.M.=252



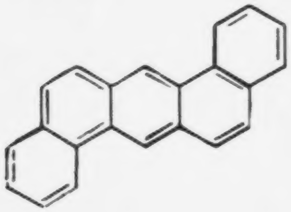
BENZO(a)PYRENE
A.M.=252



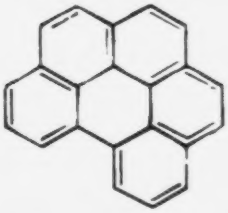
INDENO(1,2,3-C,D)PYRENE
A.M.=276



DIBENZ(a,h)ANTHRACENE
A.M.=278



BENZO(g,h,i)PERYLENE
A.M.=276



BENZO(b)FLUORANTHENE
A.M.=252

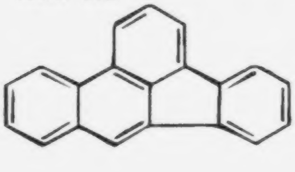


Figure 2.1. The Sixteen Priority PAHs

(from Merck Index, 1989, and Aldrich Handbook of Fine Chemicals, 1995) and Pollard, 1993).

Fortunately, in the case of PAHs, there are many microorganisms which degrade these compounds and do not produce more hazardous intermediates (Stieber *et al.*, 1990; Mueller *et. al.*, 1989). A study in Stockholm, Sweden found *Pseudomonas cepacia* was capable of degrading most of the PAHs found in creosote (Ellis *et al.*, 1991). A fungus, *Phanerochaete chrysosporium*, was found to degrade all the major PAHs in anthracene oil, which is a product of the fractional distillation of coal tar (Fetter, 1993). The initial steps in ring cleavage of some PAH compounds are shown in Figure 2.2.

Microbes used for laboratory tests have been taken from sites where creosote contamination exists. The ability of indigenous microbes to degrade PAHs is strong evidence for the potential success of bioremediation of creosote contaminated sites.

Another requirement of successful bioremediation is the existence of appropriate environmental conditions. These include such factors as soil temperature, soil pH, soil moisture, adequate nutrients, and soil structure (Birnstingl *et al.*, 1990). In terms of temperature, each microorganism has an optimal temperature for effective metabolism, and a range of temperatures over which activity is possible. A widely fluctuating temperature environment may be harmful to maintaining a stable, active population. Soil pH is generally in a range in which soil microorganisms can survive, but extremely acidic or alkaline soils may inhibit microorganism activity (Hrudey and Pollard, 1993). Fortunately, temperature and pH may be relatively easily manipulated in controlled conditions and suggested optima for hydrocarbon degradation are established (Song *et al.*, 1990).

Soil moisture is crucial to effective biological degradation. Enough moisture must be present to ensure transport of contaminants and degrading enzymes between the microbial population and the contaminants. Saturated moisture conditions may not permit sufficient oxygen transfer to support aerobic microorganisms, which are primarily responsible for degradation of aromatic hydrocarbons, when substantial degradation and oxygen consumption occur (Robinson, 1994).

Soil structure affects bioremediation in that it controls the water regime, aeration status, soil temperature, and workability. Soil particles provide the soil surfaces at which

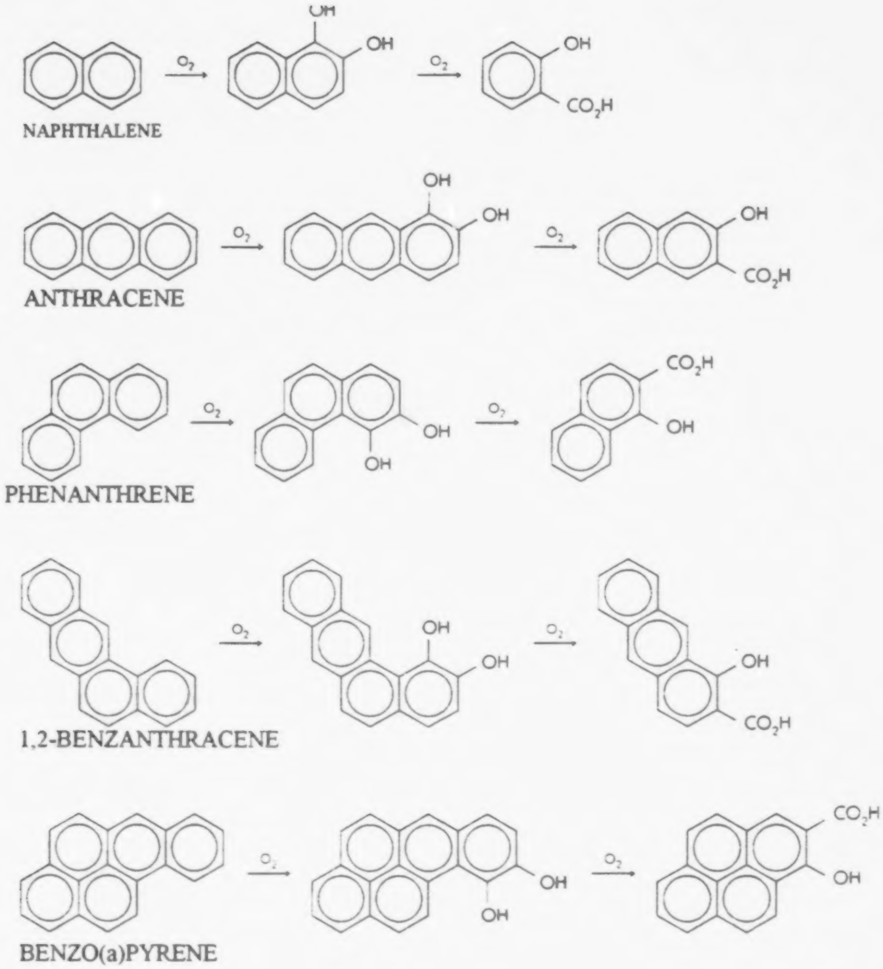

NAPHTHALENE
ANTHRACENE
PHENANTHRENE
1,2-BENZANTHRACENE
BENZO(a)PYRENE
O_2
OH
CO_2H

Figure 2.2. Initial Steps of Ring Cleavage of Some PAHs

(Adapted from Fetter, 1993)

biodegradation occurs. Fine grained soils have high surface areas, however, they are subject to low hydraulic conductivity and are thus not amenable to effective aeration. Microbial degradation in fine grained soils may be slowed also because of poor bioavailability of nutrients (Hrudey and Pollard, 1993). Bioavailability refers to the fraction of substrate available for microbial degradation.

A diagram depicting the thirteen primary possible locations in which contamination may reside in a soil matrix is shown in Figure 2.3. (Lyman *et. al.*, 1992). These locations are listed as follows:

(1) contaminant vapor as a component in soil gas (unsaturated zone)
(2) liquid contaminant sorbed to "water-dry" soil particles (unsaturated zone)
(3) contaminants in aqueous phase around soil particles (unsaturated zone)
(4) contaminants sorbed to "water-wet" soil particles (either zone)
(5) liquid contaminant caught in pore spaces between particles (saturated zone)
(6) liquid contaminant caught in pore spaces between particles (unsaturated zone)
(7) light non-aqueous phase liquid (LNAPL) floating on water table
(8) contaminant in aqueous phase in saturated zone
(9) contaminant sorbed to colloidal particles in water (either zone)
(10) contaminant diffused into mineral grains of rocks (either zone)
(11) contaminant sorbed onto or into soil microbiota (either zone)
(12) contaminant in aqueous phase of mobile pore water (unsaturated zone)
(13) liquid contaminant in rock fractures (either zone)

For PAHs in soil, only some of the thirteen possible locations are occupied by PAH contamination. To better understand why PAHs reside in certain locations and not others, some background information on the sixteen priority PAHs is required.

Table 2.1. provides information on the PAHs including their average molecular mass, aqueous solubility, boiling point, log K_{ow} and K_{ow} values, and some observed health effects. The K_{ow} value is called the octanol-water partition coefficient, and is correlated with the sorptive affinity to soil organic matter of the compound of interest (Dudas, 1994). K_{ow} does not have units, rather, it is meant to provide a ratio of the amount of compound that partitions to the soil phase versus the amount of compound that partitions

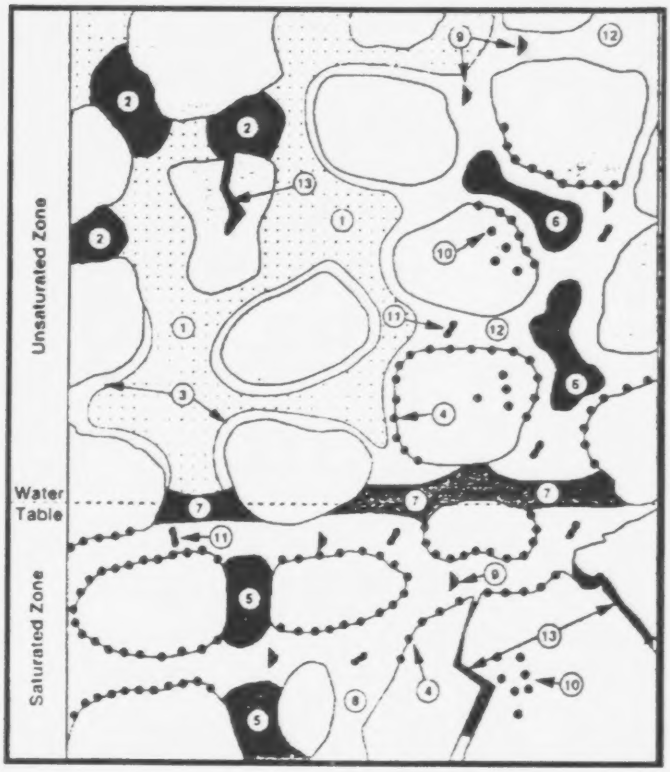

Unsaturated Zone
Water Table
Saturated Zone
9
12
2
2
13
2
1
6
10
1
11
12
6
3
4
7
7
7
11
9
5
13
10
4
8
5

Figure 2.3. Thirteen Possible Locations of Contamination in Soil

(Adapted from Lyman *et.al.*, 1992)

Table 2.1. Properties of the Sixteen Priority PAHs

PAH Name	Average Molecular Mass	Aqueous Solubility (mg/L)	Boiling Point (°C)	Log K_{ow}	K_{ow}	Comments
Naphthalene	128.16	31-34	217.9	3.81	6500	
Acenaphthalene	152.00	3.93	280	4.66	45700	
Acenaphthene	154.21	3.93	279	4.67	46800	Irritant.
Fluorene	166.21	1.90-1.98	295	4.96	91200	
Phenanthrene	178.22	.816-1.29	340	5.24	174000	On Toxic Substances List.
Anthracene	178.23	.73-1.29	340	5.28	190000	
Fluoranthene	202.26	.260-.265	384	5.78	603000	
Pyrene	202.24	.135-.160	404	5.99	977000	
Benz(a)anthracene	228.28	.010-.014	437.6	6.98	9550000	Highly toxic; cancer suspect agent
Chrysene	228.29	.002-.006	448	7.40	25100000	Suspected carcinogen; mutagen
Benzo(b)fluoranthene	252.32	0.001	-	7.95	89100000	
Benzo(k)fluoranthene	252.32	0.001	-	7.95	89100000	
Benzo(a)pyrene	252.30	.0030-.0038	495	7.49	30900000	Carcinogenic in animal experiments
Indeno(1,2,3-c,d)pyrene	276.00	0.062	536	6.44	275000	
Dibenz(a,h)anthracene	278.33	-	524	-	-	Suspected carcinogen; mutagen
Benzo(g,h,i)perylene	276.00	0.00026	>500	8.49	30900000	

List compiled from Zemanek (1994), Aldrich Chemical Co. (1994), and Merck Index, 11th Edition (1989)

K_{ow} =octanol:water partition coefficient (octanol represents an organic medium)

Log K_{ow} and K_{ow} values calculated based on an approximation equation, Dudas (1994) to the aqueous phase. K_{ow} and aqueous solubility are inversely related, that is, a relatively high K_{ow} value indicates relatively low aqueous solubility and high sorption affinity for soil. The K_{ow} values in Table 2.1. were calculated based on an approximation equation, therefore, they are not precise values and only provide an indication of the relative sorptive ability for soil organic matter for that particular compound.

It is important to note some trends derived from the table. Molecular mass and aqueous solubility are generally inversely related, that is, the higher the molecular mass the lower the aqueous solubility. The PAHs have relatively high boiling points, which may be approximately inversely correlated to their relative volatilities. That is, PAHs with high boiling points have low volatilities. Boiling point temperature increases with increasing atomic mass. Aqueous solubility varies from 0.0003 mg/L to 30 mg/L, a variation of 100,000 times. The K_{ow} values likewise vary over a wide range of 50,000 units. The implications of these wide variations is that within the sixteen priority PAHs, there is a broad spectrum of behavior. Any management strategy is therefore complicated, since it must attempt to accommodate these widely varying behaviors.

Returning to the locations of creosote contamination in the soil regime, creosote is a dense, non-aqueous phase liquid or DNAPL (density greater than water and non-aqueous phase refers to the relative insolubility of creosote in water) which means it sinks through the soil. As the creosote pool migrates downwards, it leaves a trail of residual creosote behind it. This residual creosote may be located in both the unsaturated and saturated zones. The forms of this residual include all thirteen locations, except not as LNAPL floating on the water table because creosote is a DNAPL and only marginally as contaminant vapor (naphthalene is the most prominent vapor from creosote). Given the low solubilities and high adsorptive affinities of some of the PAHs, the majority of the creosote exists as oil-phase creosote and sorbed contaminant, with only small percentages of the total concentrations found in aqueous phase. Work by Zemanek showed the approximate percentages of PAHs in each phase as approximately 70-95% in the oil (creosote) phase, 5-30% sorbed to soil, and less than 1% in the aqueous phase (Zemanek, 1994).

Microbes degrade compounds mainly in the aqueous phase or at the aqueous phase/oil phase interfaces (Robinson, 1994). However, partitioning of contaminant to the aqueous phase is severely limited by oil-phase partitioning, adsorption, and rate-limiting diffusion processes (Pollard *et al.*, 1993, and Mueller *et. al.*, 1989). It has been found that the residual oil phase in soil is approximately 10 times more effective as a sorptive phase than natural organic matter in soil (Boyd and Sun, 1990). To improve the potential for biodegradation to occur in a soil, the amount of creosote accessible to the aqueous phase must somehow be increased, that is, the bioavailability of the contaminant must be increased (Stieber *et al.*, 1990).

The foregoing discussion suggests the potential for soil freezing. The primary hypothesis for this thesis is that freeze-thaw processes in soil may provide a mechanism by which PAH contamination in soil is made more bioavailable. It is suspected that soil freeze-thaw cycles may assist in the degradation and reduction in toxicity of the hydrocarbons in the soil phase (Cummings *et al.*, 1994). The rationale for this concept is developed in the following section.

2.3. Literature Review of Relevant Research

2.3.1. Structural Effects due to Freezing and Thawing Soils

As Figure 2.3. showed, contaminants may be located in many places in soil, such as coating soil particles, trapped in dead end pores, or held between soil grains due to capillary forces (Fetter, 1993). If a mechanism reorganized soil grains and particles, this may free some contamination which was previously trapped in dead end pores, or held between soil grains. Soil freezing is one process which can cause such changes.

Many studies have been done to examine structural changes and soil particle reorganization caused by freezing and thawing of soils. Alternate freezing and thawing cycles have been shown to change soil physical properties, such as the grain size distribution (Iskandar, 1986).

As early as 1931, extensive study on the nature of frost action in soils was conducted and showed that freezing causes either aggregation or dispersion of soil particles, with the nature of ice crystallization a determining factor on soil behavior (Baver, 1956). It was later reported that alternate freezing and thawing causes a granulating action on soil clods, which breaks the clods apart and causes structural changes in the soil matrix (Baver, 1956).

Chamberlain and Gow (1979) performed a study on four different fine-grained soils to study effects of freezing on vertical permeability, examining soil structure before and after freezing. They found freezing and thawing increased permeability as much as 100 times, and caused significant structural changes in the soils they examined. For soils where clay particles predominate, vertical shrinkage cracks were found which were attributed to high negative pore water pressures that develop during freezing. For coarser grained soils where more angular silt or sand particles exist, increased permeability likely resulted from a reduction in the volume of solids in the pore spaces of the soil. This is illustrated in Figure 2.4. The top schematic illustrates a clayey silt (larger particles predominate), and the reduction in volume of solids in the pore space of the soil found after freezing. The lower schematic illustrates a silty clay (small particles dominate), and again, reduction of volume of solids in the pores is predicted.

A study was conducted on the effect of freeze-thaw cycling on the permeability and structure of compacted clay soils used for caps and barriers on waste sites (Chamberlain *et al.*, 1990). The soil permeability increased by 30-50 times following freezing. The changes in permeability were attributed to structural changes in the soil caused by freezing and from increases in the degree of saturation. Structural changes were found to occur on a microscopic scale where scanning electron photographs showed large voids appearing where there was previously a relatively homogenous structure. Also, macroscopic cracks appeared.

Another study on permeability of compacted clay after freezing found that permeability greatly increased for soils which were compacted wet of optimum. For these samples, permeability increased 70-300 times following freezing. The increase was

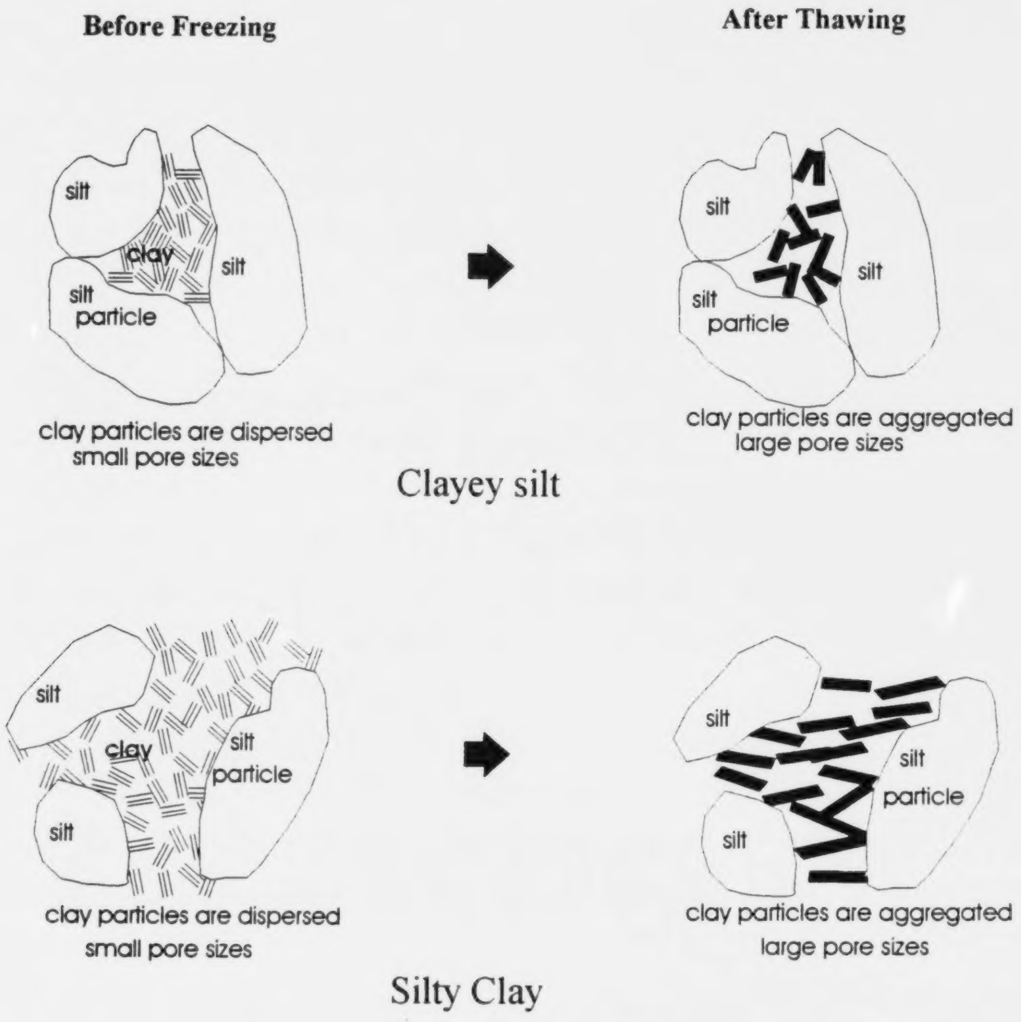

Before Freezing
After Thawing
silt
clay
silt
silt
particle
silt
silt
silt
particle
clay particles are dispersed
small pore sizes
clay particles are aggregated
large pore sizes
Clayey silt
silt
clay
silt
particle
silt
silt
silt
particle
silt
clay particles are dispersed
small pore sizes
clay particles are aggregated
large pore sizes
Silty Clay

Figure 2.4. Hypothesized Structural Changes due to Freezing and Thawing

(After Chamberlain and Gow, 1979)

attributed to cracking in the clay caused by ice lenses. More ice lenses tend to form with wetter soils (Kim and Daniel, 1994).

A study by Coutard and Moucher (1985) to identify criteria representative of the effect of repeated freezing and thawing cycles on a laminated silt loam used a very slow freezing rate (ambient air temperature set to -5°C) and thin section analysis was done on frozen soil. Vesicles and platy structures were found in the frozen soil, created by ice segregation. Very narrow nearly vertical cracks were also found, which were created by mechanical stress within the frozen soil. Mild cooling applied over 18 freeze-thaw cycles was found to be sufficient to produce a wide range of new structures and microfabrics in the laminated silt loam they tested.

A study to determine the effects of freezing and thawing on the structure of a saturated clayey silt slurry consolidated with a wide variety of initial porosities was conducted by Konrad (1989). Changes in soil structure were examined by direct measurements of vertical hydraulic conductivity and analysis of unidirectional freezing laboratory tests. While there was no evidence of vertical crack features in any of the frozen soil samples, hydraulic conductivity generally increased which indicates some structural changes occurring. Konrad hypothesized that the mechanism of structural change was not necessarily at the advancing frost fringe, but rather in the colder zone behind it from -0.4°C to -0.57°C. As the ice front advanced, existing ice in macropores traveled deeper into pore space, thus reducing capillary free water. Temperature and pressure pushed ice into micropores, causing reduction of water film thickness around clay minerals. Since freezing of the remaining water films around the clay minerals occurred in a confined manner, the 9% expansion volume change of the water films during phase transformation from water to ice caused structural rearrangements in both soil micro- and macro-pores. After thawing, particles did not move back into original arrangements, and permanent changes were left in the pore-size distribution characteristics.

Stepkowska and Skarzynska (1989) found that freezing cycles influenced the microstructure of clays, causing parallel particle arrangements, an increase in particle thickness and grain size, and changes in aggregation state and macropore formations.

These changes depend on the mineral composition of the soil. In the silty clay used for their study, grain size analysis following freezing confirmed the increase in aggregate size.

While it has been shown that freezing and thawing affect soil physical properties, the type and magnitude of effects reported have not always been consistent. Some studies show soil freezing causes a breakdown of soil physical properties, while others show freezing improves physical properties. Another study showed that freezing may have a positive or negative effect on a soil depending on the soil involved, the initial water content and degree of aggregation, and rate of freezing (Sillanpaa and Webber, 1961). The effect of freezing on physical properties of a soil, including soil structure, are the result of complex actions and interactions of initial soil conditions and freezing temperature (Benoit and Voorhees, 1990).

For the purposes of this research, it is the structural changes in soil caused by freezing which were expected to increase availability of creosote in the soils which were studied. The structural changes of interest included the breaking apart of dead-end pores and shifting of soil grains holding creosote between them. These changes were hypothesized to increase the creosote availability and accessibility for biodegradation.

2.3.2. Hydrocarbon Mobility Studies in Frozen and Thawed Soils

Much of Canada and the northern United States experiences freezing and thawing cycles in the active layer of soil. The active layer is the layer in soil subject to annual winter freezing and summer thawing (Tsytovich, 1975). As a direct result of increasingly stringent regulations governing the safe disposal of hazardous wastes and the high costs of site remediation in North America, it is important to understand if and how contaminants move in frozen and intermittently frozen ground (Cummings *et al.*, 1994).

The U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) has undertaken several studies in the past decade seeking to understand the behavior of contaminants in freezing soil. The objective of one study was to evaluate freezing-induced volatile organic contaminants (VOC) movement in soil as a potential technique for in-situ soil decontamination (Ayorinde *et al.*, 1986). Soil columns were artificially spiked with a mixture of chloroform, benzene, and toluene, three VOCs. Test columns were frozen while control columns were left unfrozen. Freezing took place over 14 days, with an average rate of 0.25 cm per day. Following freezing, the samples were thawed and determination of VOC concentrations in all samples was performed. A reduction in concentrations of contaminant was found in the frozen samples, with less contamination found around the bottom portion of the samples than the top. This indicates that the contaminant moved upwards in the soil, possibly through exclusion from the aqueous phase in the direction of the advancing frost front. Exclusion occurs when ice freezes and pushes solutes out of the ice into available remaining water (Iwata *et. al.*, 1988). As the VOC moves upwards to the soil surface, some of it volatilizes into the air. The researchers found that compounds with lower octanol-water partition coefficients (K_{ow} values) showed larger decreases in soil-phase concentration compared to compounds with higher K_{ow} values. This agrees with theory, since a low K_{ow} indicates a low affinity for the soil phase.

Another study by the U.S. Army CRREL was set up to evaluate and analyze the possibility of mobilizing different types of contaminants by freezing in a silt. Contaminants investigated included six explosive residues found at U.S. Army ammunition plants, as well as VOCs such as chloroform and toluene. Concentration profiles were determined for frozen and unfrozen control soil columns. Samples were frozen from the bottom upwards. One freeze cycle at a very slow freezing rate, 0.5 cm/day held constant throughout the experiments, was used. Moisture content was also held constant. For three explosives, freezing did not reduce the concentrations and for the other three explosives and chloroform and toluene, a concentration reduction was observed in the range of 20-40% following freezing. The inherent volatility of VOCs, the soil spatial heterogeneity, and the complex chemical interactions between the organic compounds and the soil particles represent some of the sampling problems and difficulties encountered in the use of artificial freezing as a potential soil decontamination method (Ayorinde et al., 1989).

Another study compared the concentrations of four VOCs: benzene, chloroform, toluene, and tetrachloroethylene, in frozen and unfrozen silt. The silt was spiked with the

VOCs, and separated into a control group (unfrozen) and the test group (frozen). The test group was frozen once at a rate of 2-3 cm per day. Following freezing, the concentrations of the VOCs were determined for the test and control samples. Freezing had not moved the VOCs ahead of the frost front, but rather retarded the volatilization of each organic in the frozen soil relative to the unfrozen soil (Taylor *et. al.*, 1990).

The evidence from the above studies is not conclusive. However, given the evidence of hydrocarbon movement induced by freezing found in some studies (Ayorinde *et. al.*, 1986), the possibility of creosote movement induced by freezing was tested as part of this thesis. The hypothesis was that freezing and thawing a creosote contaminated soil may induce movement of the creosote through the soil in the direction of the advancing freezing front.

2.4. Discussion of Significant Variables

The size and structure of soil aggregates resulting from the freezing and thawing process is dependent on many factors, including moisture content, rate of freezing, lowest temperature the soil was exposed to, the type of minerals and ions present, and the initial particle arrangement before freezing (Chamberlain, 1989). A discussion of some of the more significant variables follows.

2.4.1. Moisture content

Certain moisture conditions are essential to obtain maximum structural reorganization induced by freezing and thawing. Research which examined the dispersion and aggregation of soil after freeze thaw-cycles demonstrated that the water content of the soil at freezing directly affects soil structure (Baver, 1956). Kim and Daniel (1994) in their examination of the effects of freezing on permeability found that the largest increases in permeability caused by freeze-thaw were for specimens compacted at or wet of the optimum water content (which is a relatively high water content). The hydraulic conductivity increased 70-300 times in specimens compacted wet of optimum, whereas in specimens compacted dry of optimum, hydraulic conductivity was only increased 2-6 times. The increase in hydraulic conductivity was due to changes in the soil structure.

Increases in permeability greater than 10 times occurred when freeze-thaw cycling was initiated at an initial water content just below their liquid limit (Chamberlain *et al.*, 1990). As initial water content approached the plastic limit, which is a lower water content than the liquid limit, much smaller increases in permeability were observed. Pawluk (1988) performed a study to determine whether or not microfabrics in a naturally occurring soil could be reproduced experimentally through artificial freezing and thawing. The most marked changes in soil fabric were observed where soil moisture content was at or slightly above field capacity, which is a relatively high level of moisture content.

All of the previous discussion suggests that maximum structural reorganization effects caused by freezing occur when the moisture content is relatively high, with much lesser effects being found when moisture content is lower. Because an objective of this thesis is to optimize the availability of creosote contaminants, moisture content was examined as a variable. Based on knowledge of soil behaviour and the review of previous research, freezing coupled with a high moisture should bring about maximum soil structural changes which may cause more PAHs from creosote to become available to the aqueous phase.

2.4.2. Freezing rate

Another variable which significantly affects soil structure reorganization because of freezing is the rate at which the freezing front advances, or rate of freezing. One researcher found that ice crystallization controlled the resulting structural changes in frozen soils, and crystallization is influenced by the rapidity of cooling (Baver, 1956).

Research by Brewer and Pawluk (1975) expanded on these ideas. A major study on arctic and subarctic soils was performed which found that slow freezing forms ice crystals in tension-free pore space, which act as crystal growth centers. These centers result in a permanent enlargement of pore spaces. Rapid freezing forms many crystal growth centers which subsequently break down aggregates.

In a study performed by the Cold Regions Research and Engineering Laboratory (CRREL) to quantify parameters which influence contaminant transport in soils during freezing, freezing rate was found to be the most significant of the influencing factors (Ayorinde *et al.*, 1986).

Chamberlain (1989) found that freezing rate had an effect on the size of micro-aggregates formed. Rapid freezing caused a decrease in the size of micro-aggregates formed, and slow freezing increased micro-aggregate size.

The above research indicates that overall, slow freezing increases aggregation of soil particles and rapid freezing appears to break apart aggregates. Therefore, in an attempt to optimize the release of trapped creosote, freezing rate was examined as a variable for the freezing conditions. The hypothesis was that a rapid freezing rate should break apart soil aggregates more effectively than a slow freezing rate, thus freeing trapped creosote contamination more effectively.

2.4.3. Sample Density

None of the reviewed literature indicated that structural reorganization effects in soils induced by freezing were dependent on the initial density of the soil. Therefore, density was not examined as a variable for the experiments. Efforts were made to keep the density as constant as possible for all soil samples.

2.4.4. Freezing end point temperature

Some work has been carried out to determine the effects of freezing end point temperature on soil restructuring caused by freezing. Chamberlain (1989) found that structural changes in the soil fabric continued as the temperature of the soil was lowered, even though little or no moisture movement was occurring. However, the maximum structural changes were found after the initial freezing. Therefore, for this experiment, freezing end point temperature was not examined as a variable, but was held constant to achieve both slow and rapid freezing. These temperatures are discussed in more detail in the discussion on Experimental Set-up in Section 3.3.3.

2.4.5. Number of freezing cycles

In a study performed by Chamberlain and Gow (1979) to determine the effects of freezing and thawing on vertical permeability, freeze-thaw cycling was repeated until little or no change in the void ratio or permeability occurred which generally took only 3 cycles. Ayorinde and Perry (1989) performed a study on the movement of 3 explosive residues in frozen soil. They concluded that after only one freeze-thaw cycle, the maximum effects had taken place.

Stepkowska and Skarzynska (1989) found an increase in soil particle thickness and the formation of aggregates occurred in frozen soil after only one freezing-thawing cycle from temperatures of +16°C to -5°C. Chamberlain (1989) found that the largest change in soil structure by freezing occurs during the first freeze-thaw cycle, with much smaller changes occurring with successive freeze-thaw cycles. Chamberlain and Blouin (1977) studied the effects of freeze-thaw cycles on dredged materials. They found that after one single freeze thaw cycle, significant effects were seen as the permeability of fine material increased because of structural changes in the soil matrix.

Based on the above discussion, maximum structural effects from freezing appear to be achieved consistently through one freezing cycle. Therefore, only one freezing cycle was used for the soils frozen for this thesis.

2.5. Experimental Hypotheses

Based on the literature review, the hypotheses which this thesis tested are:

(1) the freezing and thawing of a creosote contaminated soil increases the availability of the PAHs from creosote to the aqueous phase;

(2) freezing may induce movement of the creosote through the soil in the direction of the advancing freezing front;

(3) freezing with a high soil moisture content will have a significantly greater effect than a low soil moisture content in terms of causing increased PAH availability;

and

(4) a rapid freezing rate will be significantly more effective than a slow freezing rate in causing increased availability of PAHs following freezing.

2.6. Hypothesis Testing

The hypotheses testing for this thesis include one factorial analysis and one analysis of variance (ANOVA) test.

Factorial analysis was selected because it is one of the most efficient ways to analyze the effects of several factors. For this thesis, a two-level factorial analysis was used, which requires the factors of interest to be set to two levels. The benefits of using a 2-level factorial are:

1. Relatively few runs per factor studied are required. While factorial analysis does not explore a wide region of factor space, it is very useful for indicating *major trends* in experimental results.
2. When a more thorough exploration is required, factorial analysis can easily be augmented to form composite designs.
3. Interpretation of observations is through relatively simple arithmetic.
4. Factorial analysis offers the ability to test the effects caused by each factor, called the *main effects,* as well as any interaction between variables called *interaction effects.*

(Box, *et.al.,* 1978).

The ANOVA analysis will test whether freezing the soil caused a significant release of PAHs compared with an unfrozen control soil.

The factors which will be tested in the factorial analysis are:

- contaminant movement- data for the "bottom" and "top" of the frozen soil
- soil moisture content- data for a "high" and a "low" level
- freezing rate- data for a "fast" and a "slow" level

The experimental set-up is discussed in detail in Section 3.6.

3.0. METHODS AND MATERIALS

3.1. Soil Sampling

The objective of soil sampling is generally to obtain reliable information about a particular soil (Canadian Society of Soil Science, 1993). For the purposes of this thesis however, the objective of soil sampling was simply to obtain a uniform, homogenous soil for use in the experiments. As variables inherent to the soil would not be accounted for, it was important that the soil be as uniform as possible.

The initial criteria for the soil samples was to obtain one with a relatively low level of contamination (between 1-5%), and one with a relatively high level of contamination (between 10-20%). This was to determine whether effects from freezing were significant in both a high and low level contaminated soil.

A soil with a low level of creosote contamination was relatively easy to locate and obtain since there exist several sites in Alberta with low levels of creosote contamination. A site visit was conducted, and a sample obtained from the surface layer of a creosote-contaminated site which is currently undergoing partial remediation. The sample was analyzed to determine the total petroleum hydrocarbon contamination (TPHC) level, which was found to be approximately 1-1.5% TPHC. Grain size analysis showed that approximately 30% of the particles fell in the clay-size range, with the remaining in the silt-size range (results of grain size analysis are found in Section 4.2). The Department of Renewable Resources at the University of Alberta homogenized the sample in a cement mixer at their Ellerslie Research Station. The sample was then taken to another laboratory where it was stored at 4°C. It was removed from storage on an as needed basis.

A site with a high level of contamination (high being 10-20% TPHC) was more difficult to locate, since there are relatively few highly contaminated sites in Alberta. Two soil samples were obtained from Dr. Phil Fedorak in the Department of Biological Sciences at the University of Alberta. These samples were found to have a sufficiently high level of contamination of 12-15% TPHC. When a larger sample from the original site was obtained, however, the received sample was found to contain an extremely high level of contamination, approximately 40% TPHC. As this level of contamination was much too high, a site visit to collect a suitable sample was conducted. A sample was collected from approximately a 1 metre depth, and was found to have 12-15% TPHC. This sample was stored in two 20 litre buckets at room temperature for approximately 1 month, and was then moved to a 4°C storage room. The soil was then sieved through a 0.945mm sieve and homogenized by mixing as it was sieved. It was then returned to the 4°C room for storage, and subsamples were removed from storage on an as needed basis.

3.2 Soil Characterization and Variable Quantification

3.2.1. Determination of Total Petroleum Hydrocarbon Contamination Levels

Total petroleum hydrocarbon contamination (TPHC) levels were determined through a Soxhlet extraction procedure following the method used by Zemanek (1994). Methylene chloride was chosen as the solvent based on a study of its effectiveness as a solvent for hydrocarbon extractions (Martin *et al.*, 1991; and McGill and Rowell, 1980).

To prepare a Soxhlet extraction , approximately 5-15g of soil was placed in a Whatman cellulose extraction thimble. The thimbles used were single thickness, with an inner diameter of 35 mm and external length of 80 mm. The Supelco surrogate standard (for quantitation purposes) was added at this time. The surrogate standard is made up of five deuterated PAH compounds: naphthalene d8, acenaphthalene d10, phenanthrene d10, chrysene d12, and perylene d12. Masses of surrogate standard used varied from 40 μg to 140 μg. A glass wool plug was placed over the soil in the thimble, to prevent tiny soil particles from being carried into the extracted solvent, and the thimble was placed in the Soxhlet extractor tube. A 250 mL glass flask containing 150 mL of solvent was placed under the extractor tube, and the flask and tube were connected to a condenser apparatus. The solvent was heated to evaporation, and the condenser caused the solvent to condense as a liquid in the extractor tube. This continued until the tube fills to the level of a draining channel, at which point the solvent siphons back into the glass flask. In this manner, the soil was repeatedly washed with the solvent for a period of 12-16 hours to facilitate dissolution of the oil in the soil.

After extraction was complete, the extract was passed through an anhydrous sodium sulfate drying column to eliminate any water present. The water-dried extract was then subjected to rotary evaporation to eliminate some of the solvent and reduce the total volume. The extract was washed into a 50mL volumetric flask, and brought up to volume with fresh solvent. This quantity was placed in a storage vial, and moved to a 4°C refrigerator to eliminate losses by evaporation.

For the TPHC determination, three 10 mL aliquots were removed from the storage vial and each was placed in a shallow, pre-weighed aluminum evaporating dish. Any remaining solvent evaporated in a fume hood over approximately 24 hours. The aluminum dishes were then reweighed, and by difference, the mass of hydrocarbon residual oil was determined:

$$\%\ \text{Oil} = \left(\frac{\text{M.D.E.} \times \text{F}}{\text{M.S.}}\right)$$

where M.D.E=mass of the dried extract (TPHC oil-phase residue)

F = fraction of original extract, in this case, 50mL/10 mL = 5

M.S. = mass of soil placed in the thimble

The percent oil (or % TPHC) by the above formula is based on wet weight of soil. The percent oil can be expressed per dry weight by correcting the weight of soil for the original water content present in the soil. Water content determination is presented in the following section.

3.2.2. Moisture Content Determinations

Soil water content is one of the most commonly performed kinds of soil analysis. Soil water content affects to such a great degree the behavior and use of a soil that almost every type of soil study requires measurement of water content (Carter, 1993). In Section 2.4, the third hypothesis is that a high moisture content coupled with freezing will cause significantly greater changes in the aqueous availability of creosote as compared to a low level of moisture content coupled with freezing. To test this hypothesis, moisture content must be varied with at least two levels studied.

The low level chosen is the in-situ moisture content of the soil, and the high level is in the range of the determined field capacity of the soil. The method by which these levels are determined follows.

3.2.2.1. In-situ Moisture Content

The low level of water content is set as the in-situ water content of the soil. Water content is most commonly determined through a gravimetric-drying process, as described in Methods of Soils Analysis (Black, 1965). This process suggests using a drying oven at 103°C. Another method in Soil Sampling and Methods of Analysis (Carter, 1993) suggests using an oven temperature of 105°C. However, at any temperatures above 100°C, organic matter oxidation, volatilization, and decomposition may be excessive. Therefore, it may be necessary to compromise or correct in some manner for these loss conditions (Black, 1965).

One method of correction was used by Zemanek (1994). To correct for volatile losses, a raw soil sample was placed in a 103°C oven and dried over a 24 hour period. The mass lost from this method was attributed to 100% loss of water plus 100% loss of volatile organic compounds (volatile under 103°C). An air dried aliquot of a Soxhlet extract was also placed in the 103°C oven for 24 hours. The mass loss of this sample was attributed to 100% loss of organic volatile compounds (since the water has already been removed through the sodium sulfate column). The moisture content in the soil is then calculated by subtraction:

(% loss water and % loss due to organic contaminant volatiles)
- (% loss due to volatiles x % organic contaminant present)
= (% loss water)

As an example, assume the percentage loss due to moisture and volatiles is found to be 20%. The percent loss due to volatiles only is found to be 10% of the organic extract mass, and the percent of organic contaminant present is 10% of the total mass. Therefore, the percentage loss due to volatile compounds is 1% (10% of 10%) of the total mass. If 20% of the mass of the sample is due to moisture and volatiles, then 19% of the mass is due to moisture alone when the volatiles are subtracted.

An experiment to determine the moisture content of the highly contaminated sandy soil was carried out. The percent loss due to organic volatiles and water was found to be 10.2% for three replicate samples. After Soxhlet extraction, the percent loss due to organic volatiles only was found to be 7.4%. The percent TPHC in this sample was determined to be 11.3%. The calculation follows:

$$
\begin{array}{l}
\quad 10.2\ \%\ \text{loss due to water and volatiles} \\
-\ \underline{(7.4\%\ \text{loss of volatiles in organic extract} \times 11.3\%\ \text{organics})} \\
\quad = 9.36\ \%\ \text{moisture content}
\end{array}
$$

Through this calculation, the percent loss due to volatiles for the soil sample is only 0.84%. This value represents less than 10% of the total loss due to water and volatiles.

Because of the relatively small significance of the volatile component of moisture content determination and the level of difficulty in determining moisture content accounting for volatiles (that is, performing a Soxhlet extraction to determine % TPHC for each sample), the volatile organic component was not accounted for when moisture contents were determined. This assumption is discussed further near the end of Section 3.2.2.1.

For the clay soil, the volatile component would be even a smaller fraction than for the sandy soil since the contaminant level is approximately 10 times lower.

Volatilization, on its own, is a difficult process to monitor and control. By the nature of soil analysis, there is a certain amount of unavoidable inherent error due to volatilization. For example, the sieving process introduces a degree of volatilization that is unaccounted as well as exposing the sample to air while preparing the Soxhlet extraction.

Sample drying time must be carefully monitored. Even the storage method permits uncontrolled volatilization to occur. The samples for this experiment were stored in 20 litre pails, with the soil surface covered by a plastic sheet. However, the surface soil undergoes more volatilization than the soil at the bottom of the bucket. This is unavoidable, and cannot be accounted for. Laboratory errors limit the accuracy of moisture content determinations, since leaving the soil samples exposed to air for varying times affects the amount of room-temperature volatilization that occurred and is unaccounted for. Controlling the oven temperature was difficult, since oven temperatures were found to vary by up to 10°C when placed at the same temperature setting. A final source of error is that soil is never entirely homogenous, and the amount of contamination in organic soils may vary widely even over small distances because of slight differences in topography and density of the soil (McGill and Rowell, 1980).

The method used in this thesis of calculating the water content follows:

$$\%\text{moisture} = \left[\frac{(\text{mass of wet soil}) - (\text{mass of dry soil})}{\text{mass of wet soil}}\right]$$

In the standard method for calculating moisture content, the divisor is the mass of dry soil (Craig, 1987; Liu and Evett, 1984). However, a value for moisture content was required fairly quickly for the gas chromatography/mass spectrometry (GC/MS) system software, therefore, the above equation was used to calculate moisture content because the dry mass of soil (which involves a 24 hour drying period) was not required.

The results of in-situ moisture content determinations was an average value of 6.3% for the sand, and an average value of 11.3% for the clay. These averages are based on 36 replicates and do not account for the losses from volatile organics.

An additional check for the percentage weight loss from volatile organics is the following calculation. Assume an average level of 15% TPHC (a generous assumption) present in the sand, and assume the percentage due to volatile compounds is 7.4 % (as found earlier) of the TPHC. The percentage of the total mass due to volatile organics is then $15\% \times 7.4\% = 1\%$. Given that the average in-situ moisture content for the sand was

6.3%, the volatile organics component represents a fraction of 17.5% of the mass due to moisture. While this is not an insignificant quantity, it was decided that volatile organic losses due to heating would not be accounted for as they may vary widely from sample to sample, it would introduce more analysis for each sample (i.e. a Soxhlet analysis for each sample to determine the level of TPHC), and an error of 17% in the moisture content determination was acceptable.

3.2.2.2. Field Capacity

The second level of water content, the "high" level, is chosen based on the field capacity of the soil. Field capacity is commonly defined as the amount of water retained in the surface soil after excess water has drained away through gravity (Black, 1965; Jury *et al.*, 1991; and Tan, 1994). For many coarse-textured soils, the amount of drainage occurring approaches insignificant levels within a few days. At this point, field capacity has a practical value. Finer textured soils do not show an abrupt change in drainage rate as do the coarser soils, and it is therefore more difficult to define the time at which field capacity occurs in fine textured soils. In any case, the significance of drainage from a soil varies from application to application, and therefore no universal criterion may be developed to define when to neglect downward drainage from the soil (Jury *et al.*, 1991).

Field capacity is also a measure of the soil water potential. There can be enormous spatial variability in soil water potential, and a representative average might require many measurements. The non-homogeneous nature of soil water is likely to, for many cases, outweigh inherent errors to a particular measurement technique (Carter, 1993). Therefore, an approximation of field capacity was adequate for this experiment.

Various methods exist for field and laboratory determinations of field capacity. A field procedure was modified and tested. This method involved saturating a soil in the field for a total of 2 days, and then allowing the soil to drain under gravity. The amount of water which remained in the soil after a given amount of time was the field capacity, or moisture holding capacity of the soil (Black, 1965). Another method describes keeping 50 g of fresh soil "overnight" with 100 mL of water in a filter funnel plugged with glass wool to retain the soil, and the filter funnel end stoppered. The excess water is later drained away, and soil sample is removed after a 3 hour draining period. The water holding capacity of the soil is calculated from the water retained by the soil minus the in-situ water content (Harding and Ross, 1964). Another method saturated the soil for a period of seven days in excess distilled/deionized water, then loaded 100 g samples on to a prewetted filter and allowed the water to drain under gravity. Water contents were determined once the water flow halted (Zemanek, 1994). It is important to note that no universal criterion may be developed to decide when to neglect downward drainage.

Through preliminary experiments to determine field capacity, it was found that by saturating the soil for 24 hours as opposed to one week produced greatly different results. Also, simply pouring the water over the soil and allowing it to sit for 24 hours produced different results from totally saturating the soil by tumbling it and mixing it in excess water for 24 hours.

The method finally adopted to determine field capacity involved tumbling the soil in water saturated conditions for 24 hours to thoroughly wet the hydrophobic oil-coated soil particles, and then pouring the soil/water mixture into a prewetted glass fiber filter. The soil drained until no more water dripped out, approximately 1-2 hours. The soil was then placed in a shallow, pre-weighed aluminum evaporating dish and moisture content was determined. The result is expressed as field capacity of the soil.

For the sandy soil, field capacity was found to be 14.2%. Field capacity was verified by an independent laboratory, Norwest Labs. They obtained a value of 10.0% initially. However, upon examination of their methods, it was found that no effort was made to account for volatilization in the drying process nor any attempt to saturate the soil taking into account the hydrophobic oily surfaces which greatly reduce the degree of saturation achievable by the soil. They did not mix the soil in water either.

For the clayey soil, the value obtained in-house was 39.2%. Again, Norwest was contracted to verify this value. They performed the test twice because the first time, the value obtained was very low (approximately 8%, which is virtually impossible for a clay soil). The second value they obtained was 37.4%, which agrees very closely to the value obtained in-house.

3.2.3. Grain Size Analysis

Grain size analysis is a standard test performed on a soil to determine the suitability of the soil for a particular application. Also, grain size analysis can be used to predict the susceptibility of the soil to frost action (Bowles, 1992).

3.2.3.1. Sandy Soil Analysis

The grain size analysis for this soil was performed following the method in Engineering Properties of Soils and their Measurement (Bowles, 1992) and ASTM Standard Methods D 422-63 (ASTM, 1988).

The standard mechanical method of analysis was performed by running the soil through a series of sieves, where the sieves are made of woven wire with rectangular openings ranging in size from 102 mm (4 inches) in the coarse series to 0.038mm (0.0015 inches) in the fine series. The sieving process does not provide information on the shape of soil grains. It only yields information on grains that can pass, given a proper orientation, through sieve openings rectangular in size. Individual particle sizes are not determined, rather, approximate size ranges are bracketed between two sieve sizes.

The soil was first extracted, to eliminate any effects caused by the creosote bonding particles together. Extracting the soil is particularly important where the TPHC level is high, since the oil present may have a bonding effect on soil grains. The total mass of the soil is weighed, and then washed over one of the smallest sieves, a 200 sieve (openings=75mm). This sieve is of the smallest practical size, being roughly the finest size that will still permit relatively free passage of water. Material passing the 200 sieve is lost (washed away), and the material that does not pass is collected and dried in a forced air oven at 105°C, and weighed. By difference of the masses, the smallest fraction of particles is accounted for.

A series of sieves which has been carefully cleaned is assembled, starting with the largest aperture opening on the top of the stack and ending with the smallest at the bottom. For this test, the sieve stack followed a typical stack arrangement. This was the lid, followed by a Number 4 sieve (4.76 mm openings), Number 10 (2.00mm), Number 20 (0.840 mm), Number 40 (0.425 mm), Number 60 (0.250mm), Number 100 (0.149 mm), Number 200 (0.074mm) and finally the bottom pan. The dried soil was poured onto the top sieve, and the assemblage of sieves and soil was placed on a shaking machine. This shakes the sieves for approximately 15 minutes. The sieves are removed, and the fraction of material or residue retained on each sieve is weighed. The sum of these weights is calculated, and compared to the total weight of the soil. A loss of more than 2% of the total weight is considered unacceptable.

The percent retained on each sieve is calculated by dividing the weight retained on each sieve by the original sample weight before washing. The percent passing is calculated by starting with 100 % and subtracting the percent retained on each sieve as a cumulative procedure. As stated earlier, sieve analysis only provides approximate size data, hence the results are presented as a curve. The data is plotted on semi-log paper. The results of the graphical analysis are presented in Section 4.2.1. for sand and Section 4.2.2. for clay, and the raw data is located in Appendix D-1.

3.2.3.2. Clay Soil Analysis

Hydrometer analysis is widely used to estimate the particle size distribution of a soil when a significant quantity of the soil particles pass through the Number 200 sieve. For the clayey soil, a hydrometer analysis was used following the method in Chapter 6 of Engineering Properties of Soils and their measurement (Bowles, 1992) and the method in ASTM Standard Methods D 422-63 (ASTM, 1988).

Hydrometer analysis utilizes the principles of sedimentation, and the relationship between the velocity of fall of spheres in the fluid, the diameter of the spheres, the specific weight of the spheres and of the fluid, and the viscosity of the fluid as expressed by Stokes Law. Stokes Law governs the velocity at which spherical particles settle in a suspension. The larger the particles, the faster they settle and the smaller the particles, the slower they settle. The law is not valid for particles outside the range 0.0002mm <=D <= 0.2mm where D=particle diameter. Grains larger than 0.2mm cause excessive fluid turbulence and very small grains are subject to Brownian movement (Craig, 1987).

Hydrometers were originally designed to measure the specific gravity of a fluid, but by altering the scale they can be used to read other values. Terms needed to solve the Stokes equation include the specific gravity of the soil and of the fluid the soil particles settle in. As well, tables of the viscosity of water are needed, and temperatures must be recorded as temperature affects specific gravity of water and water viscosity.

For this experiment, a 4% $NaPO_3$ solution was made as the dispersing or deflocculating agent to ensure that all particles settle individually. Approximately 125 mL of this solution was mixed with the soil sample, and 61.3 grams of uncontaminated clay soil and 52.3 grams of contaminated clay soil were used. Two soils were used for comparison purposes. This mixture was allowed to stand for a brief time.

After standing, the mixture was transferred to a dispersion cup (a malt mixer cup was used), and distilled water was added till the cup was 2/3 full. The cup contents were mixed rapidly with the malt mixer for 2 minutes. During mixing, a control sedimentation cylinder was prepared. This was a 1000 mL cylinder which had 125 mL of the $NaPO_3$ solution in it, and was brought up to volume with distilled water. However, no soil was added to this cylinder.

After mixing, all the contents of the dispersion cup were transferred to the sedimentation cylinder. The cup was washed clean into the sedimentation cylinder. Then, the 1000 mL cylinder was brought to volume with distilled water. The temperatures of the sedimentation cylinder and control cylinder were found to be within 1°C of each other, which is the desired limit. The sedimentation cylinder was capped with a rubber stopper, and agitated for 1 minute (agitation being inverted and righted every second for 1 minute). It was placed righted on the counter, and the stopper was carefully removed. Sediment on the stopper was washed into the cylinder.

The first hydrometer reading was taken at 1 minute after setting the cylinder down. Another reading was taken at 2 and 4 minutes. Then, the cylinder was capped with the stopper and agitated again. Readings were again taken again at 1, 2, and 4 minutes. It was found that the two sets of readings agreed with each within one unit on the hydrometer.

This ensures the suspension is mixed adequately and that readings are reproducible. The first few readings are heavily dependent on how well the suspension is mixed.

Readings were taken subsequently at 8, 16, 32, and 64 minutes of elapsed time. After 64 minutes, readings were taken as convenient. Readings were taken over three days, after which time the solution was washed into an evaporating dish. The dish was placed in a forced air convection oven at 100°C to evaporate all the water from the samples. The remaining residue was weighed. The residue was also collected and used to determine the specific gravity of the soil. Specific gravity of the soil is needed to solve Stokes equation to determine the soil particle size diameters. A value of 2.65 g/cc may be assumed for specific gravity, however, a check on this value was performed.

Theresa Cloake of the Geotechnical Engineering division of the Department of Civil Engineering at the University of Alberta processed the collected hydrometer values using a computer software package. The particle size diameter data was estimated by this program.

Ms. Cloake also checked the specific gravity of the sample following the method in Chapter 7 of Engineering Properties of Soils and their measurement (Bowles, 1992). In this method, approximately 60 grams of air dried soil was mixed with water in an evaporating dish to form a creamy paste. The paste was transferred to a malt-mixer container, and water was added to make approximately 200 mL of soil-water mixture. This was mixed for 5-10 minutes. A dry 500 mL volumetric flask was weighed, and carefully filled to the volume mark with de-aired water. With the water level at the volume mark and the neck inside the volume mark dry, the flask was weighed and recorded as W_{bw}. A temperature reading was taken to ensure the soil-water mixture was not more than 1°C different from the de-aired water. The soil-water mixture was transferred to the volumetric flask, and all the soil was washed into the flask. Sufficient temperature-stabilized water was added so that the flask was about two thirds full. The flask was attached to a high vacuum for a minimum of ten minutes. The flask was gently agitated and turned during this time. When the de-airing was complete, de-aired temperature stabilized water was added to the flask until the bottom of the meniscus was exactly at the volume mark. The neck of the flask above the calibration mark was dried. The flask and its contents were weighed to obtain the quantity W_{bws}.

The flask contents were then emptied into an evaporating dish, ensuring none of the soil was lost, and this was oven dried. The oven dried soil was weighed to obtain the quantity W_s. The specific gravity, G_s, of the soil was computed using the following equation:

$$G_s = \frac{alpha \times W_s}{W_{bw} + W_s + W_{bws}}$$

where the values are as defined in the above discussion, and alpha is the temperature correction coefficient, computed from:

$$alpha = \frac{\text{gamma at T}}{\text{gamma at } 20^\circ\text{C}}$$

where "gamma at T" is the unit weight of water at the temperature of the test, and "gamma at 20°C" is the unit weight of water at 20°C.

This procedure was repeated until values of G_s agree within 2% of each other. The final value determined was 2.66 g/cc, which is very close to the value of 2.65 g/cc which may be assumed as the specific gravity.

The grain size distribution curves for the clay samples are found in Section 4.2.2, and the raw data is located in Appendix C-1.

3.3. Controlled Freezing Methodology

There were four components to the freezing program for the experiment. The first involved compacting the soil using standard methods, and calculating the soil density. The second was the actual freezing of the soil. The third component was monitoring the temperature of the soil during freezing, and determining the rate of freezing from the collected temperature data once the freezing test was complete. The final component was thawing the sample.

3.3.1. Soil Sample Density and Compactive Procedure

3.3.1.1. Sandy Soil

None of the reviewed literature found soil density to be a significant factor affecting soil restructuring following freezing. Therefore, the soil density was not examined as a variable but rather was maintained constant throughout the experiments.

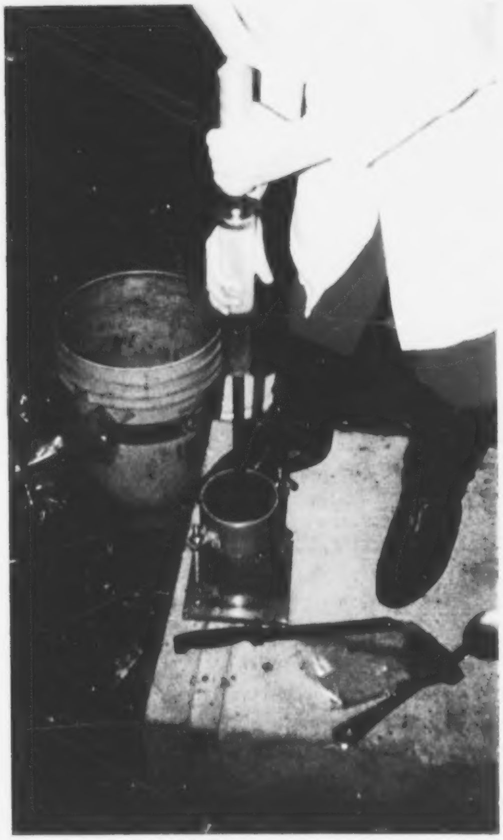
The sandy soil was compacted to a constant density through a Standard Compaction technique. This technique followed method ASTM D 698-78 (1988). Necessary equipment included a cylindrical steel mold, 101.6mm in diameter with a capacity of $944 \pm 11 cm^3$. The base plate assembly as well as the extension collar are constructed so they can be securely attached and detached from the mold. The extension collar extends above the mold at least 50.8mm. The steel rammer weighs 2.49±0.01kg and has a circular contact face with a diameter of 50.8±0.13mm. The rammer falls freely through a distance of 304.8±1.6mm from the surface of the soil.

For the low moisture content samples, soil was removed from the storage bucket and placed directly in the compaction mold. For the high moisture content samples, the mass of soil required to fill the mold was pre-weighed, and enough tap water was added to the soil to raise the moisture content to the desired level. The soil and water was thoroughly mixed to ensure a uniform moisture content. Standard procedures would involve equilibrating the soil with the added water for a period of 24 hours, however, this procedure was not followed in the interest of saving time. Following the moisture content adjustment, the soil was placed in the compaction mold.

Each specimen was compacted in three layers of approximately equal height. Each layer was hit 25 times with the compaction hammer and the hammer was moved around over the whole soil surface to ensure uniform compaction. During compaction, the mold rested on a concrete cube weighing not less than 91 kg. Care was taken during compaction to avoid rebound of the rammer from the top end of the guidesleeve. The blows were applied at a uniform rate. Figure 3.1. shows the compaction procedure.

Following compaction, the extension collar was removed and the compacted

Figure 3.1. The Soil Compaction Procedure



specimen was trimmed with a straightedge even to the compaction cell base. The base plus the soil was weighed, and the mass of soil was calculated by difference from the original base mass. The soil was extruded out of the cell using a hydraulic jack, and the compacted soil sample was taken to be frozen.

3.3.1.2. Clay Soil

The procedure for the clay soil was slightly different than for the sandy soil. There was not as much clay soil available for use as the sandy soil, therefore, risers were inserted in the compaction cell to reduce the total volume of soil compacted (the overall height of soil in the mold was approximately halved). The mold, collar, rammer, and method of moisture addition all had the same description as for the sandy soil.

To hold the soil density constant, the compaction process was not constant between the low moisture and high moisture samples. The low moisture content samples were compacted with 15 blows on each of 2 layers of soil of approximately equal height. For the high moisture content samples, the number of blows required to compact the sample varied from 5-15 blows on each of 2 layers of soil of approximately equal height. The sample was then extruded from the compaction cell using a hydraulic jack, and was weighed without the compaction base. Using an approximate moisture content, the density was calculated immediately following compaction. If the density did not fall within range of the desired value, the sample was recompacted. If the density was acceptable, the sample was then frozen.

3.3.2. Freezing process

The freezing apparatus consisted of two halves of a plastic cylinder 10cm in diameter and 15 cm high with a Teflon liner approximately 5 mm thick. The cylinder was split, having two equal sides which, when put together, made the whole cylinder. Figure 3.2. shows the freezing cell with the two halves apart. The compacted soil was placed on a steel base at the bottom of the cell, which was outfitted with brass couplings and tubing

Figure 3.2. The Freezing Cell with a Compacted Clay Sample

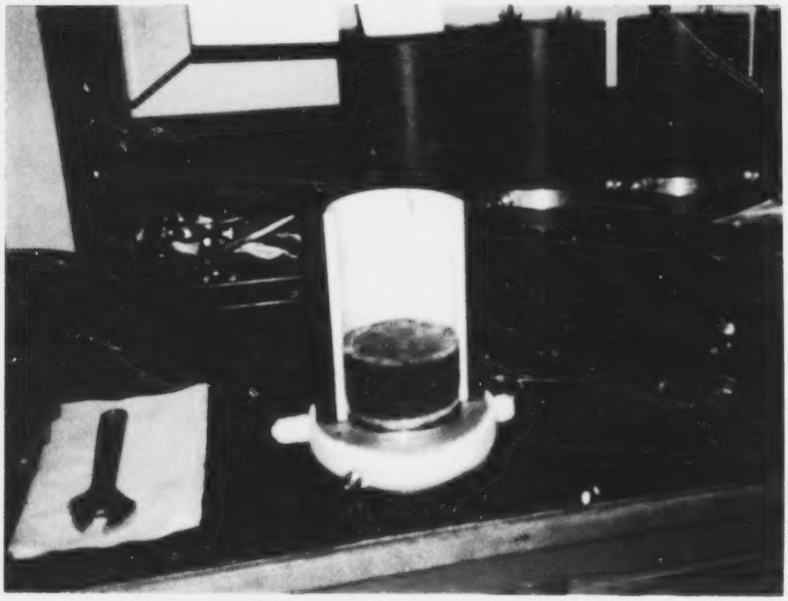
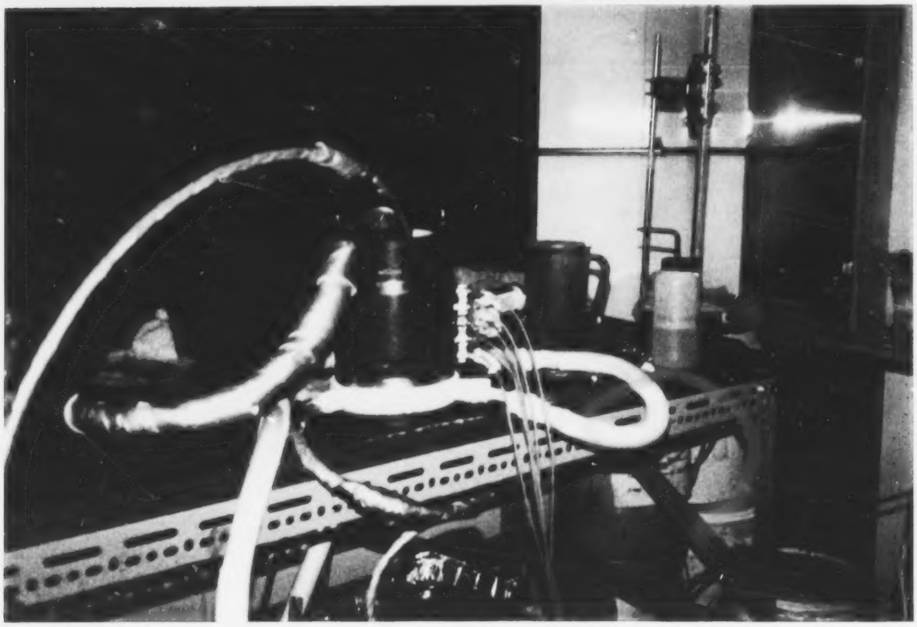


Figure 3.3. Freezing Cell Duing the Freezing Process



in the base through which ethylene glycol circulated to regulate the temperature of the base. The two half sides were then fastened together, and a steel top cap fit inside the cylinder and rested on the soil surface. The top cap was, like the bottom base, fitted with brass couplings and tubing to permit ethylene glycol to circulate through it, regulating the temperature at the top of the cell.

Two separate baths of ethylene glycol were temperature controlled, one for the top cap and one for the base of the cell as previously described. The baths could achieve temperatures in the range of room temperature to -15°C. Different freezing rates were attained by varying the temperature of the top cap and bottom steel base. The "fast" setting was achieved by setting the bottom plate to approximately -15°C, and the top plate to approximately -2°C. The "slow" setting was achieved by setting the bottom plate to -5°C and the top plate to -2°C. The top plate was set to a temperature below zero in order to freeze the top of the soil. In initial testing, the top of the cell was covered with a piece of insulation in an attempt to eliminate large heat transfers from ambient air to the soil. The freezing temperature at the bottom of the soil was expected to cause a temperature gradient in the soil permitting the top soil to freeze. However, although the ambient air temperature in the room was only 4°C, the soil would not freeze at the top without artificial cooling applied. Hence, freezing the entire sample required placing the top cap at -2°C on the top soil.

The controlling temperature was the bottom plate since preliminary testing found extreme heat losses occurred between the top plate and the soil. The soil at the bottom took on more closely the temperature of the bottom steel base. Heat losses through the bottom plate existed, however, they were much lower than losses at the cell top. The temperature settings of the ethylene glycol baths are discussed in Section 3.3.3.

3.3.3. Temperature Monitoring and Freezing Rate Determination

The determination of freezing rates was made through the use of five resistance temperature devices or RTDs connected to one side of the freezing cell . In Figure 3.3. the RTDs are clearly visible on the outside of the cell. As the soil in the cell was a maximum of 10 cm deep, the RTD devices were placed at every 2 cm of depth. The Labview program was custom designed for temperature monitoring by Mr. Roy Gitzel of the Geotechnical Engineering division of the Department of Civil Engineering at the University of Alberta, and allowed temperature in the freezing cell to be monitored for any time interval. Temperature was monitored every five minutes for six hours, and then every half hour to an indefinite time. Based on the temperature profile obtained, the overall rate of freezing of the cell was determined by calculating the average rate at which the temperature drops in the soil. Figure 3.4. shows a sample freezing rate graph which was obtained from the freezing rate data. The actual freezing rates were determined by determining the slope of the initial section of the freezing curve, where the temperature decreases rapidly from approximately 15°C to -2°C.

The bottom plate was set to -15°C for the "fast" freezing rate, and set to -5°C to -8°C for the "slow" freezing rate. The top cap was held constant at -2°C to ensure the entire sample froze.

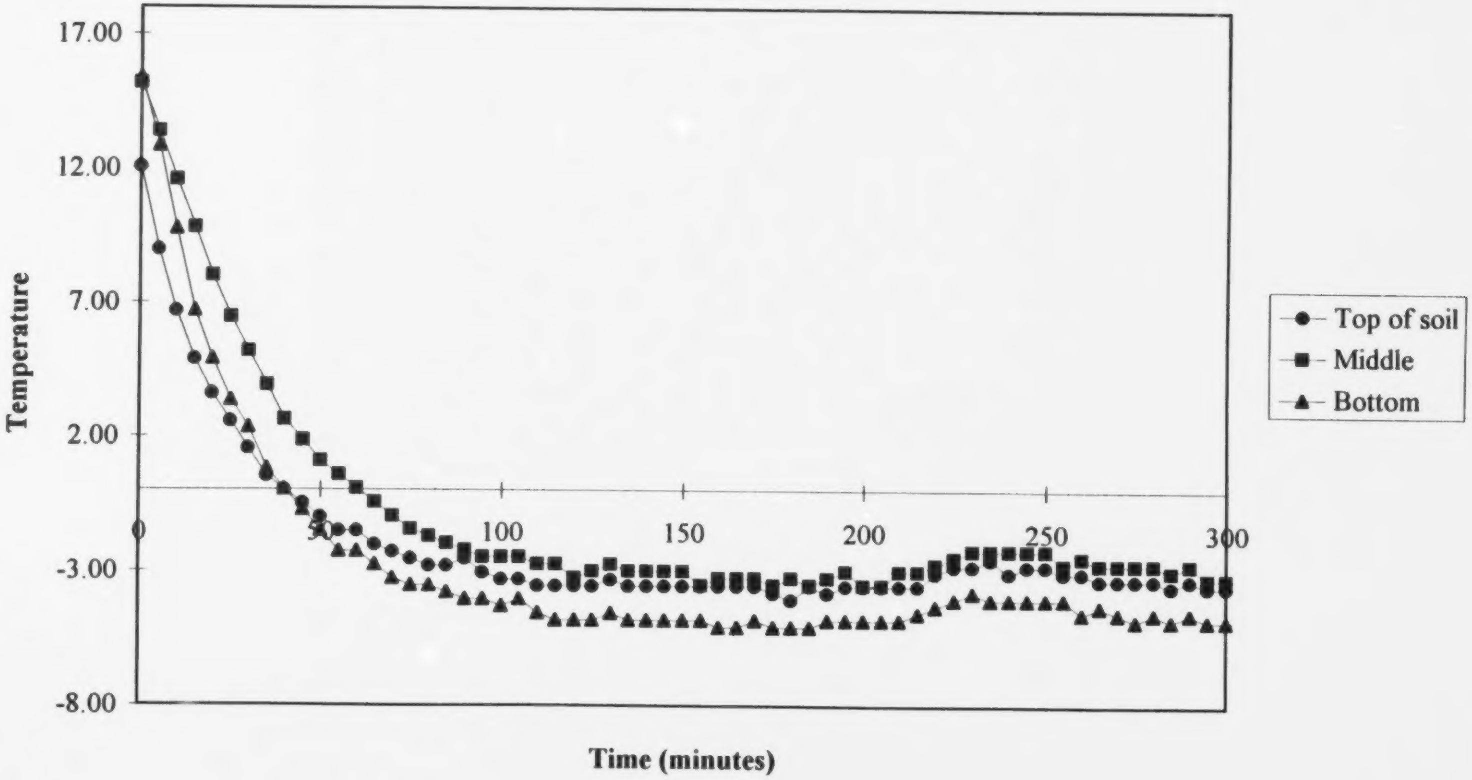
3.3.4. Thawing

Once it was certain that the samples were completely frozen through the entire sample by examining the temperature results from the thermistors, the freezing cell was disconnected from the freezing apparatus and removed from the cold room. The soil sample was removed from the freezing cell, and left at room temperature (approximately 21°C) to thaw. It was assumed that all the soil samples thawed in the same manner and at approximately the same rate.

3.4. Quantitative PAH Determinations

The quantitative PAH determinations involved determining aqueous phase concentrations, as well as oil phase concentrations. The steps outlined in obtaining these concentrations are outlined in the following sections.

Figure 3.4. Sample Freezing Rate Graph



3.4.1 Aqueous Phase PAH Determination

3.4.1.1. Aqueous Phase Batch Equilibrium

To quantify the amount of water soluble compounds available to the aqueous phase under controlled laboratory conditions, aqueous batch extraction procedures were performed on the soil samples. A batch study was chosen for many reasons. Batch and column methodologies have both been widely applied in the evaluation of waste leaching and chemical attenuation of leachates. However, the two methods differ in one important aspect: batch involves a continuously stirred batch reactor and column involves an unstirred continuous-flow reactor. Solid particles are dispersed and suspended throughout an aqueous study of a batch reactor, whereas solid particles become packed into a porous matrix for a column study. Batch experiments are generally easier to perform, more economical than column studies, and may show more reproducible data. Batch experiments are commonly performed by placing the solid material (e.g. soil) in an aqueous suspension, then equilibrating the suspension under controlled conditions with agitation, and then measuring aqueous phase concentrations to estimate release from solid to liquid (Batelle Pacific Northwest Labs, 1991). These types of experiments require care of the gas phase to which the sample is exposed during equilibration, as well as rigorous phase separation techniques following equilibration to ensure suspended colloidal material does not bias aqueous phase measurements (Voice *et al.*, 1983).

Four experimental run conditions were established (these are discussed in detail in Section 3.6), with varying levels of moisture content and freezing rate. Each experimental run condition was tested in triplicate. That is, three separate samples were subjected to compaction, freezing and thawing, and subsequent chemical analysis for each of the four run conditions. This means a total of twelve runs (three replicates of four sets of conditions) were conducted. For each experimental run, batch extractions were done in triplicate for each of three cases: unfrozen soil, and frozen soil at the bottom and top of the sample.

Batch extractions were done on three separate soil samples taken from the bulk bucket of soil before freezing, providing the "before freezing" aqueous phase PAH concentrations. These three soil samples were taken from the bucket alternately with the soil removed for compaction so that the "before freezing" sample was as homogenous as possible and representative of the soil which was frozen. Another three soil samples were taken randomly from the top centimetre of the compacted sample after it was frozen and thawed, providing data for "after freezing" and for the "top" of the soil sample. A final three soil samples were taken randomly from the bottom centimetre of the compacted soil after it was frozen and thawed, providing data for "after freezing" and for the "bottom" of the soil sample. This number of samples was required to make "before" and "after" freezing comparisons, as well as creosote movement determinations between the frozen and thawed soil sample "bottom" and "top".

The above discussion indicates that a total of nine soil samples were taken for each experimental run, and batch extraction and subsequent PAH quantitation was performed on each of the nine samples. As stated earlier, a total of twelve experimental runs were conducted (three replicates of four conditions). With nine extractions performed on each run, a total of 108 extractions and subsequent chemical analyses were performed for each soil studied. That is, 108 individual analyses were performed for the highly contaminated soil, and 108 analyses for the low level contaminated soil. By replicating batch extractions in triplicate and replicating experimental run conditions in triplicate, an adequate estimate of the error involved in this experiment should be obtainable.

Before the batch equilibrium tests could be started, the mass of soil to be used for equilibration with the water was determined to ensure that the level of contamination present not exceed the solubility limit of the PAHs. If PAH solubility was exceeded, any increase in PAH availability would not be detectable because the relative concentrations of PAHs in the aqueous phase would not be able to increase above the soluble limit.

Therefore, preliminary testing was done to ensure masses of soil used contained a sufficiently low mass of PAHs. For both soils, several soil:solvent ratios were established and tested. The results of these tests are found in Table 3.1. for sand and Table 3.2. for clay. Based on the data in these tables, a soil mass of approximately 10 g for sandy

Table 3.1. Soil:Solvent Ratios for Sand

Solid: solvent	Grams soil used	µg PAH/ gram soil	Total PAHs extracted (µg)
1:10	24.98	47.93	1197.31
	25.08	50.89	1276.50
	25.02	61.79	1546.22
1:15	16.78	64.10	1075.87
	16.47	69.07	1137.92
	16.67	68.56	1142.88
1:25	10.19	67.23	685.06
	10.00	63.16	631.57
	10.17	70.43	716.38
1:50	5.10	106.73	544.31
	5.14	84.88	436.14
	5.05	92.60	467.25

Table 3.2. Soil:Solvent Ratios for Clay

Solid: solvent	Grams soil used	µg PAH/ gram soil	Total PAHs extracted (µg)
1:10	22.35	12.52	279.88
	22.43	12.07	270.69
	22.24	11.46	254.83
1:15	14.74	20.8	306.55
	14.94	18.66	278.73
	14.83	18.64	276.44
1:25	9.33	29.33	273.62
	9.06	26.01	235.56
	9.01	28.61	257.83
1:33	6.50	35.64	231.80
	6.80	31.93	217.16
	6.44	41.38	266.53
1:50	4.48	68.62	307.42
	4.45	55.00	244.69
	4.45	52.88	235.21
1:100	2.28	97.89	222.80
	2.81	64.41	181.19

soil and approximately 2.5 g for clay ensured the mass of PAHs was under the aqueous solubility limits.

Each batch equilibrium test was performed by placing the known weight of soil in a 250mL glass bottle, and filling the bottle with pH-adjusted deionized water. The bottle was completely filled to the top by dropping water from a pipette into the bottle so that the meniscus concaved upward. Ensuring the bottle was completely full minimized contact of the aqueous phase with the gaseous phase which would interfere with aqueous phase partitioning from the soil. Deionized water was used to reduce the possibility of sample contamination. The pH of the water was adjusted to facilitate improved extraction, since the PAH fraction is more easily removed by high pH water (APHA, AWWA, WEF, 1992). The pH was adjusted to >11 using a standard NaOH solution.

The bottle was sealed, inverted to check for leakage, and then placed on a tumbler which equilibrated the sample for 24 hours. The bottles used are shown in Figure 3.5., and the tumbler used is shown in Figure 3.6. The equilibrium time of 24 hours was chosen following the method used in Lee *et.al.* (1992a) for a study of diesel fuel equilibration in water, and also as used in Lane and Loehr (1992) for a study of PAH aqueous phase equilibrium concentrations. After 24 hours, the bottles were removed from the tumbler and processed through liquid/liquid extraction.

3.4.1.2. Liquid/liquid Extraction of the Aqueous Phase

After tumbling, approximately 50mL of aqueous suspension was drawn out of the soil/water mixture in the bottle, and placed in a 50mL centrifuge tube. The suspension was centrifuged for 10 minutes at 1500 rpm to settle out sediments and interfering suspended particles. After centrifugation, the liquid was ready for aqueous extraction. Extraction was performed as described in Technique 8 in Modern Experimental Organic Chemistry (1982). Exactly 40mL of the centrifuged water was placed in a separatory funnel, which is a specially designed funnel for extracting compounds from solution. Most organic compounds are more soluble in water-insoluble organic solvents, such as dichloromethane or ether, than they are in water. Therefore, an organic compound which

Figure 3.5. Batch Equilibrium Bottles

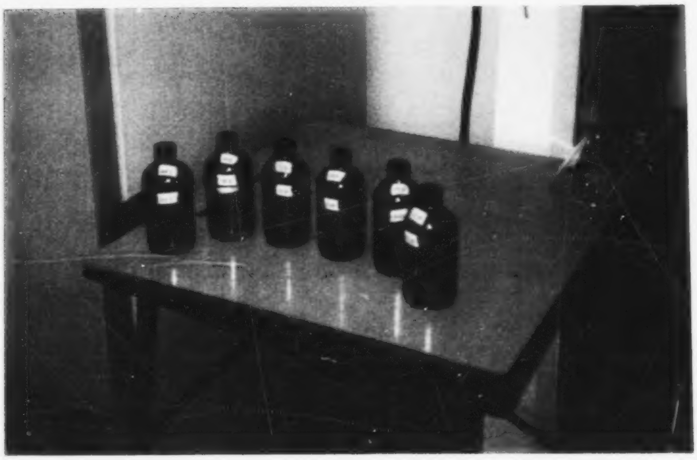
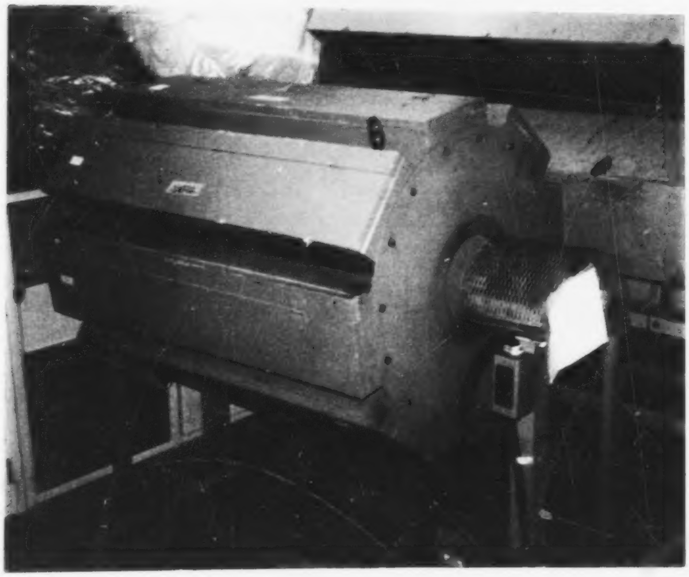


Figure 3.6. Tumbler Apparatus



is in the aqueous phase will readily partition between water and solvent when mixed in a separatory funnel. 15 mL of dichloromethane (density of 1.34g/mL) was added to the funnel, and 1.6 μg of the Supelco 5-compound deuterated standards (which is discussed in the Quality Assurance section) were also added at this time. The liquids were mixed by gently inverting the funnel several times, and venting the gases as required for 2 minutes. The solution settled for approximately 10 minutes, after which the solvent phase was drained from the funnel and collected. The process was repeated twice again from the point of solvent addition. By repeating the extraction, 95% of the solvent-soluble compounds are removed in the first extraction, leaving 5% solvent-soluble compounds. Another 95% of the solvent-soluble compounds are removed in the second extraction, leaving 0.25% solvent-soluble compounds. Another 95% of solvent-soluble compounds are removed in the third extraction, which leaves 0.0125% solvent-soluble compounds. By using three extractions, 99.9875% of the total amount of solvent-soluble compounds are theoretically extracted from the aqueous phase.

The solvent phase collected was filtered through an anhydrous sodium sulfate column, which served a dual purpose. The sodium sulfate eliminates any water present in the dichloromethane, and also filters out clumps of interfering suspensions. The solvent phase was collected in a 250mL flask, then heated on a rotary evaporator to reduce the overall volume of liquid. The remaining solvent phase was transferred to a gas chromatography (GC) vial, with the flask contents carefully rinsed into the vial to avoid sample losses. Just prior to GC injection, an internal standard of deuterated anthracene was added to the vial. This internal standard is discussed further in the Quality Control section. The vial contents were subjected to gas chromatography/mass spectrometry (GC/MS) analysis for quantitation of the PAHs of interest.

3.4.1.3. GC/MS Analysis of the Extract

Concentrations of the 16 Priority PAH compounds in the aqueous phase extracts were determined using a Hewlett Packard 5890 gas chromatograph (GC) and 5970 mass selective detector (MSD). The GC used a 30m long x 0.25mm inside diameter fused silica chromatographic column with a 0.25μm film thickness (J&W Scientific, DB1301). The temperature ramping method and carrier gas linear velocity had been predetermined by Sandra Kenefick and Mike Zemanek. The method follows Zemanek (1994). An initial temperature hold of 70°C for 4 minutes was set, allowing the solvent to evaporate. This was followed by a thermal ramp of 70°C to 280°C at 10°C per minute, with a helium carrier gas column head pressure of 80kPa resulting in good peak definition. A second temperature ramp of 280 to 300°C at a rate of 5° C per minute was set, and the final temperature of 300°C was held for 5 minutes to permit elution of low volatility compounds that remained on the column.

The major ion (for quantitation) and two minor ions (for confirmation) of each PAH of interest were monitored using the selected ion monitoring option (SIM), which reduces interference from other compounds. Quantitation of analytes of interest was based on the signal response of the major ion as compared to the signal response of one of the five deuterated internal standard ions (Supelco catalogue #4-8902). Each ion of interest representing a PAH compound was quantified by multiplying its specific peak area by the ratio of the concentration of the internal deuterated standard, to its specific peak area. The formula for quantitation is:

$$\text{Concentration, } \mu g/L = \frac{(A_c) \times (I_s)}{(A_{is}) \times (R.F.) \times (V_e)}$$

and A_c=area of compound of interest

I_s= amount of surrogate standard added, ug

A_{is}= area of surrogate standard

R.F.= response factor

V_e= volume of liquid extracted, L

Response factors which had previously been determined by Zemanek (1994) were used for quantitation. New response factors were calculated, however, there were several problems with these factors as discussed in Section 4.5.5.

3.4.2. Quantitative Oil Phase PAH Determination

3.4.2.1. Soxhlet Extraction

The in-situ concentrations of the 16 priority PAH compounds in the native soil were required to determine if there was enough PAH in the soil for aqueous extractions to show detectable results. The base concentrations were also used to compare the aqueous phase PAH concentrations to the soil phase PAH concentrations. Determining these base concentrations in the soil involved several steps. The soil was first subjected to Soxhlet extraction to remove all of the hydrocarbon compounds. This procedure was described in section 3.2.1. Then , an aliquot ranging from 0.5mL to 5 mL was removed from the storage vial of the extract. This aliquot was then processed through a two-step sample clean-up procedure described below.

3.4.2.2. Soxhlet Extract Clean-up Process

The clean-up procedure involved running the extract aliquot through a series of chemicals which extract interfering compounds. This is referred to as selective PAH adsorption/elution by adsorption media column chromatography. The result after the treatment is much better peak resolution on the GC/MS system.

Adsorption/elution involves loading the sample extract onto a chromatographic column and passing solvents of varying polarities through the column to selectively desorb compounds of similar polarity (Zemanek, 1994). The columns which produced the desired effects had previously been determined by Zemanek.

The first column was a 6 mL Florisil solid phase extraction (SPE) tube. The tube was conditioned with dichloromethane and care was taken to ensure the packing did not dry out before the extract was added. The extract was added and the tube was washed with two column volumes of dichloromethane. The fraction collected was subjected to nitrogen blowdown to evaporate some of the solvent, and the remaining extract was then solvent exchanged to hexane. Solvent exchange to hexane was required to change the polarity of the solution so that the desired hydrocarbons were absorbed in the next clean-up step.

An alumina column was prepared at this time. A small plug of glass wool was placed at the bottom of a 10 mm x 254 mm glass champagne column, followed by approximately 10g of 80-200 mesh alumina powder packing. The alumina was previously activated at 225°C for 16 hours prior to use. A 1 cm layer of anhydrous sodium sulfate was placed at the top of the alumina to ensure any water remaining in the sample was adsorbed to the sodium sulfate and did not remain in the sample extract. The alumina column was preconditioned with 50mL of hexane. Just before the meniscus of hexane reached the top of the sodium sulfate, the sample extract was added. The vial which contained the extract was rinsed three times into the column with 2 mL of hexane and a final rinsing of 10 mL of hexane. All eluate from the hexane application was discarded since the PAHs were adsorbed to the alumina and interfering hydrocarbons were present in the eluate.

After most of the hexane had drained from the column, 80 mL of dichloromethane was added to the column to desorb the PAHs from the alumina into the solvent. This eluate was collected in a 250 mL flask and rotary evaporated to reduce the total volume. When the volume was approximately 1 mL, the extract was placed in a GC vial for quantitation. Care was taken to wash the flask content into the GC vial so that no sample losses occurred. At this time, the deuterated anthracene internal standard was added so that recovery of the surrogate standards for that sample could be calculated.

3.4.2.3. GC/MS Analysis of the Extract

The GC/MS analysis for the "cleaned-up" extract was identical to that for the aqueous PAH extract. Please refer to Section 3.4.1.3.

3.5. Quality Assurance and Quality Control

Rigorous standards for quality assurance and quality control must be recognized and rigidly adhered to during sample collection and analysis to produce data of known and defensible quality. As a minimum, quality assurance involves validation for the parameters of accuracy, precision, recovery rate, and negligible sample contamination (APHA, AWWA, WEF. 1992). These are discussed in the following sections.

3.5.1. Accuracy

The accuracy of a given method can be determined through analysis of a series of standard samples which are subjected to the entire analytical procedure. Accepted techniques include:

1. The use of certified reference materials, or performance evaluation samples. These are samples which contain known amounts of the compounds of interest, and are supplied by an outside agency. They are analyzed as an ordinary sample and data obtained is compared to the known values, thus determining the accuracy of the analyst (APHA, AWWA, WEF, 1992). This procedure was followed for the Soxhlet extraction and subsequent clean-up procedure using a marine sediment standard issued from the National Research Council of Canada. Performance evaluation samples were used to determine the accuracy of the aqueous extractions. In this process, quantities of PAHs known to a person other than the analyst were added by that person to the aqueous media. The samples were then analyzed as an ordinary sample after which the values obtained are compared to the known values for the sample.
2. Comparison of data obtained to that obtained using a reference method of known uncertainty. This is done by comparing data to that obtained from an independent Certified Laboratory. As this method was too expensive for this project, this method of accuracy verification was not used.

3.5.2. Precision

Precision is a measure of the degree of closeness by which multiple analyses of a given sample agree with each other, and is generally reported by the standard deviation of the results (APHA, AWWA, WEF, 1992).

As discussed in Section 3.4.1.1., four sets of experimental conditions are studied. Each set of conditions was run in triplicate, producing a total of twelve sample runs. By replicating the sample runs, an estimate of the between-run error may be calculated.

A total of nine extractions and chemical analyses were performed for each of the twelve sample runs: triplicate extractions and chemical analyses for the unfrozen soil, for the frozen soil at the sample top, and for the frozen soil at the sample bottom. With nine chemical analyses performed for each of the twelve runs, a total of 108 batch extractions and chemical analyses were performed for the sandy soil and another 108 batch extractions and chemical analyses for the clay soil. By repeating the extractions and chemical analyses in triplicate, an indication of the reproducibility of extractions may be made from the standard deviation for these measurements.

3.5.3. Sample Recovery

A technique often used to indicate the efficiency of the overall method is to measure the recovery of a specific added analyte. For this experiment, a surrogate standard of five deuterated compounds (naphthalene d8, acenaphthalene d10, phenanthrene d10, chrysene d12, and perylene d12) was added as the standard for quantitation of the analytes of interest. As a check for recovery, an internal standard of deuterated anthracene was added to the sample extract immediately prior to instrumental analysis by GC/MS. The known amount of internal standard, combined with instrumental response factors, was used to determine the overall recovery of the surrogate standard. This technique permits rapid identification of samples with very poor recoveries, and identifies those samples as suspect in terms of recovery. If the standard recovery is low, it is likely that the sample recovery is also low and the sample is therefore unuseable.

3.5.4. Sample Contamination

The method of analysis should not introduce any analytes of interest to the actual sample, and this must be verified through checks for sample contamination. Checks were performed through the analysis of blanks, which are by definition, a sample matrix containing negligible or undetectable quantities of the analytes of interest present.

Blanks commonly used include field blanks, which are run to determine background pre-contamination concentrations of analytes of interest. For this experiment, no field blanks were tested.

Glassware blanks were processed through the entire method without any sample matrix or standard added to determine if there were any contaminating materials on the glassware or solvent impurities. The batch equilibrium and aqueous extraction procedure were performed with no addition of soil or standard for the glassware blanks.

Method blanks involved performing the entire method without a sample matrix added, but with the standards added. This located standard contamination, reactions, or degradation over time. This was a critically important step, since the standard was used to verify the quality of all other results.

A minimum of 5% of the sample load was recommended for analysis as blanks. This meant that for every 20 samples, one method blank was required. For this experiment, 216 sample runs were conducted, therefore, a minimum of 10 method blanks were required. In addition to the blanks already mentioned, blanks should always be run for new batches of reagents, solvents, and standards. The outcome of the sample contamination testing is discussed in detail in Section 4.6.4.

3.6. Experimental Design

3.6.1. Sandy Soil Experiment Protocol

Experimental conditions were established by using a 2^2 factorial arrangement of the variables of moisture content and freezing rate. A total of four conditions were established, and three replicate runs for each condition were performed. The run numbers (for identification purposes) and corresponding experimental conditions are described as follows:

RUN NUMBERS	Moisture	Freezing Rate
3 & 11 & 19	In-situ	Slow
4 & 12 & 20	In-situ	Fast
7 & 15 & 23	Field Capacity	Slow
8 & 16 & 24	Field Capacity	Fast

A total of 12 soil freeze/thaw runs were performed for the sandy soil.

As discussed in Section 3. 4.1.1, for each individual run, a total of nine batch extractions and subsequent chemical analyses of aqueous phase PAH concentrations were performed. The nine analyses were as follows: three replicate batch extractions and chemical analyses of aqueous phase concentrations for the unfrozen soil, three for the frozen soil at the top of the compacted sample, and three for the frozen soil at the bottom of the compacted sample. A total of 108 soil samples were analyzed for aqueous phase PAH concentration.

3.6.2. Clay Soil Experimental Protocol

Experimental runs for the clay soil were established in much the same manner as for the sandy soil. The run numbers (for identification purposes) and corresponding experimental conditions follow:

RUN NUMBERS	Moisture	Freezing Rate
1 & 9 & 17	In-situ	Slow
2 & 10 & 18	In-situ	Fast
5 & 13 & 21	Field Capacity	Slow
6 & 14 & 22	Field Capacity	Fast

A total of 12 soil freeze/thaw runs were performed for the clay soil.

As discussed in Section 3. 4.1.1, for each individual run, a total of nine batch extractions and subsequent chemical analyses of aqueous phase PAH concentrations were performed. The nine analyses were as follows: three replicate extractions and chemical analyses of aqueous phase concentrations for the unfrozen soil, three for the frozen soil at the top of the compacted sample, and three for the frozen soil at the bottom of the compacted sample. A total of 108 soil samples were analyzed for aqueous phase PAH concentrations.

4.0. RESULTS

4.1. Control of Experimental Conditions

To study the significance of variables on an outcome, it is necessary to vary only those variables while holding other factors constant. If other factors are not held constant, they may introduce experimental error into the measured outcomes and proper conclusions may not be made.

For the experiments reported on in this thesis, it was necessary to hold moisture content constant at a low level and a high level, and hold freezing rate constant at a low and high level. Frozen soil sample densities were held constant, and the freezing process was held as constant as possible. The following sections discuss the degree to which the above listed factors were held constant or at their respective level.

4.1.1. Moisture Content

4.1.1.1. Low Level of Moisture Content

The low-level of moisture content was chosen to be the in-situ moisture content of a sample, and was not artificially adjusted. The data for in-situ moisture content is found in Table 4.1.

For sand, the coefficient of variation (which is the sample standard deviation divided by the sample mean) associated with in-situ moisture content was 19.6%. This variation may involve other factors in addition to sample moisture. For example, the volatilization of organics was discussed in detail in Section 3.2.2.1., and as stated in that section, no attempt was made to account for organic matter losses. However, it is likely that the variability inherent with organic matter losses at high temperatures may account for only a small portion of the variability of the moisture content values. Also, the sand was homogenized during sieving which only permitted homogenization of a localized amount of soil. Therefore, the existence of pockets of moisture and/or contamination

Table 4.1. "In-situ" Moisture Content

	% Moisture for Sand soil (before freezing)	% Moisture for Clay soil (before freezing)
	6.32	11.70
	6.32	10.87
	7.88	10.87
	4.40	11.66
	5.63	11.40
	7.37	11.40
Average=	**6.32**	**11.32**
Standard Deviation=	**1.24**	**0.37**
Coefficient of Variation=	**19.6%**	**3.26%**

Table 4.2. "High" Level Moisture Content

	% Moisture for Sand soil (before freezing)	% Moisture for Clay soil (before freezing)
	15.63	20.19
	18.70	20.90
	16.90	20.20
	14.96	21.05
	17.09	19.90
	17.92	20.00
Average=	**16.87**	**20.37**
Standard Deviation=	**1.24**	**0.48**
Coefficient of Variation=	**7.35%**	**2.37%**

could cause large variability in moisture content.

For clay, the coefficient of variation was 3.26%. It is possible that this error is lower than that of the sand due to the better homogenization of the clay (it was homogenized in a large cement mixer). Also, the contamination level in the clay was approximately 12 times lower than the sand so volatilization of organic compounds has an insignificant role in variability for moisture content values for the clay.

4.1.1.2. High Level Moisture Content

The high level of moisture content was determined by approximating the field capacity moisture content of the sandy and clayey soils as described in Section 3.2.2.2. Then, when preparing the samples, water was added to the soil to raise the moisture content to a level near field capacity.

For both the sandy soil and the clay soil, raising the moisture content to the determined field capacities made it nearly impossible to compact the soil to any uniform density. The soil was much too soft and water-saturated. Therefore, the final values of "high level" of moisture content which were used were determined through a trial and error process. Moisture was added to the soil, and compaction was attempted. Moisture contents were finally chosen based on the ability of the soil to be compacted through a modified standard compaction procedure to the desired density. The set levels of moisture were approximately 17% for sand, and 21% for the clay.

The results of moisture content determinations are found in Table 4.2. on the previous page. For the sandy soil, coefficient of variation was 8.25%. This is less than the error for in-situ moisture content of the sandy soil, however, it is still a significant error. Possible causes for this error could be that adjusting the moisture content required great care. The soil mass had to be weighed very carefully, and a precise amount of water was added. If too much water was added, the excess could not be removed as the water was quickly absorbed into the soil. If the soil was not mixed very well, the water was not evenly distributed throughout the soil.

For the clayey soil, the error for moisture content was 2.37%. The potential sources of variability are similar to those for the sandy soil. For example, the addition of water and mixing the water into the soil introduce possible errors if too much water was added (which occurred occasionally) or the sample was not mixed well. Once the water was added, the sample did become difficult to mix as the clay became very stiff. An error of 2.37% for moisture content is very low, considering the possible sources of error for this value.

4.1.2. Freezing Rate

The freezing rate data is listed in Table 4.3. for the clay and Table 4.4. for the sand. The values for freezing rate are expressed as decrease of degrees Celsius per minute. The data was obtained by calculating the slope of the initial straight line section of the freezing rate curve as shown in Figure 3.4, where the temperature is decreasing rapidly. Freezing rate was determined for each resistance temperature device (RTD). A total of five RTDs were located in the cell every two centimeters up the side of the cell. The compacted sandy soil, all five RTD temperatures were useful. For the clay, the compacted sample was a smaller volume than that of the sand and only three of the RTD temperatures represented temperatures in the clay soil.

For the slow freezing rate for clay, the top of the soil had the highest coefficient of variation, 32%, the middle 22.6%, and the bottom 11.3%. It is expected that the top would show the largest variation, since the largest heat losses occur at the top of the soil and the smallest heat losses at the bottom. For the fast freezing rate for clay, there is much variation between samples. Run 2 and 10 and 18 had their temperatures recorded with a different type of data logging system that only recorded the temperature every two hours. If the data for these three runs is discarded, the coefficients of variation decrease significantly. Other sources of variability include variations in the constant temperature baths. Opening and closing the door to the temperature controlled room affected the temperature of the baths. Also, it was found that if the ethylene glycol circulation was shut off for a prolonged period of time, for example while the tubes for the ethylene glycol

Table 4.3. Freezing Rate Table for Clay

SLOW Freezing Rate			
Run #	Rate for Top of Sample	Rate for Middle	Rate for Bottom
1	0.209	0.257	0.287
9 & 17	0.247	0.213	0.333
5	0.361	0.317	0.318
13 & 21	0.179	0.360	0.377
Average=	**0.249**	**0.287**	**0.329**
Standard Deviation=	**0.080**	**0.065**	**0.037**
Coefficient of Variation=	**32.0%**	**22.6%**	**11.3%**
FAST Freezing Rate			
Run #	Rate for Top of Sample	Rate for Middle	Rate for Bottom
2	0.045	FAULT	0.110
10 & 18	0.073	0.093	0.079
6	0.207	0.284	0.319
14 & 22	0.293	0.361	0.535
Average=	**0.154**	**0.246**	**0.261**
Standard Deviation=	**0.116**	**0.138**	**0.212**
Coefficient of Variation=	**75.3%**	**56.1%**	**81.2%**
Omitting Runs 2,10, and 18 for FAST freezing rate:			
Average=	**0.250**	**0.323**	**0.427**
Standard Deviation=	**0.060**	**0.054**	**0.153**
Coefficient of Variation=	**24.2%**	**16.8%**	**35.8%**

Note: Units for freezing rate are: drop in °C per minute

Table 4.4. Freezing Rate Table for Sand

SLOW Freezing Rate

Run #	Rate for Top of Sample		Rate for Middle		Rate for Bottom
3	0.128	0.124	0.124	0.136	0.140
7	0.135	0.133	0.180	0.304	0.530
11	0.176	0.129	0.149	0.230	0.373
19	0.127	0.135	0.155	0.225	0.527
15	0.094	0.113	0.135	0.246	0.415
23	0.085	0.082	0.119	0.195	0.420
Average=	**0.124**	**0.120**	**0.144**	**0.223**	**0.401**
Standard Deviation=	**0.032**	**0.020**	**0.023**	**0.056**	**0.143**
Coefficient of Variation=	**26.1%**	**16.8%**	**15.7%**	**25.1%**	**35.7%**

FAST Freezing Rate

Run #	Rate for Top of Sample		Rate for Middle		Rate for Bottom
4	0.191	0.139	0.163	0.248	0.400
8	data was lost				
12	0.227	0.177	0.190	0.311	0.491
16 & 24	0.163	0.139	0.139	0.225	0.382
20	0.200	0.146	0.144	0.210	0.497
Average=	**0.195**	**0.150**	**0.159**	**0.249**	**0.442**
Standard Deviation=	**0.026**	**0.018**	**0.023**	**0.044**	**0.060**
Coefficient of Variation=	**13.5%**	**12.1%**	**14.5%**	**17.9%**	**13.6%**

Note: Units for freezing rate are: drop in °C per minute

were being attached to the freezing cell, the bath temperature decreased dramatically and only heated again once the circulation was switched back on. This contributed to erratic freezing rates. A final source of error is that the bath temperatures were changed from time to time to facilitate randomization of experimental runs, and it was difficult to obtain exactly the same temperature as achieved previously. Even if the bath was set to the exact same setting as used previously, the temperature of the bath may vary by 5°C.

For the sandy soil, freezing rate varied less than for the clay. The slow freezing rate showed more variability, overall, than the fast freezing rate. Sources of variability are the same as for the clay soil.

4.1.3. Sample Density

A constant density for each experimental run was desired to eliminate the possibility of sample density having an effect on the final results. Sample density was controlled by the standard compaction procedure for the sandy soil, and by the compactive procedure used for the clayey soil. Table 4.5. and Table 4.6. show the results of density determinations for both the sandy soil and the clayey soil respectively.

The coefficient of variation for dry density of the sandy soil was 2.37%. This value was quite low. However, given the standard method used for sample compaction, it was expected that the variability for dry density be quite low.

Dry density for the clay soil also had a small coefficient of variation, 1.95%. This error was expected for the low-level moisture content clay, since the compaction procedure was constant.

For both the sand and clay high-level moisture content samples however, compaction was performed in a non-uniform manner. Some samples were compacted with ten blows, some with fifteen, and some with only five. However, as the precise mass of soil required to fit into the compaction cell was the amount to which moisture was added, the density was kept constant more or less by fitting all the weighed soil into the compaction cell. This technique worked surprisingly well, as the overall error for density was very low for both the sand and clay.

Table 4.5. Dry Density for Sand

Run Number	Soil Mass (g)	% Moisture (unfrozen soil)	Dry Density (kg/m^3)
4	1475.1	6.32*	1489.1
12	1511.0	6.32*	1525.3
20	1432.7	7.88	1422.2
3	1446.4	4.40	1490.0
11	1454.4	5.63	1479.0
19	1488.1	7.37	1485.3
7	1558.8	15.63	1417.2
15	1618.3	18.70	1417.8
23	1634.0	16.90	1463.2
8	1595.5	14.96	1462.1
16	1631.8	17.09	1458.0
24	1613.1	17.92	1426.8
	Average Dry Density:		**1461.3**
	Standard deviation:		**34.59**
	Coefficient of variation:		2.37%

*Moisture content average of Runs 20,3,11,19

Table 4.6. Dry Density for Clay

Run Number	Soil Mass (g)	% Moisture (unfrozen soil)	Dry Density (kg/m^3)
2	662.7	11.70	1409.6
10	666.1	10.87	1430.2
18	680.6	10.87	1461.3
1	Data lost	11.66	Data lost
9	644.6	11.40	1375.8
17	673.3	11.40	1437.0
5	713.7	20.19	1372.1
13	750.4	20.90	1429.9
21	747.7	20.20	1437.3
6	736.2	21.05	1400.1
14	743.4	19.90	1434.4
22	744.7	20.00	1435.2
	Average Dry Density:		**1420.3**
	Standard deviation:		**27.72**
	Coefficient of variation:		1.95%

4.1.4. Freezing End Point Temperature

Freezing end point temperature data for clay is given in Table 4.7. The coefficients of variation for freezing end point temperature for clay ranged from 18% to 49%. For slow freezing, the middle of the compacted sample showed the greatest variation in lowest temperature reached. For fast freezing, the top of the sample showed the greatest variation. That the top of the sample would show the greatest variation is expected, since the largest uncontrollable heat losses occurred at the top of the soil sample. The bottom of the sample consistently showed the least variation, which is expected since the contact between the bottom freezing plate and the soil was good and heat losses in this location were fairly low. Other sources of variability are similar to those listed for variation in freezing rates, for example, the temperature baths did not keep constant temperatures.

The end point temperature data for the sand is given in Table 4.8. Coefficients of variation range from 10% to 53%. Again, variation near the top of the sample was consistently larger than variation at the bottom of the sample for the same reasons as listed above. Note that when Run 3 is included in the standard deviation for the runs at the slow freezing speed, the coefficient of variations are large. However, when Run 3 is not used, the variations decrease. Run 3 did not achieve very cold temperatures relative to the other runs and its temperature was significantly different from the other runs. This could be due to the operator changing the bath temperature without ensuring the proper temperature desired was actually achieved after a given amount of time.

4.2. Results of Soil Grain Size Analysis

4.2.1. Sandy Soil

The sandy soil was sieved according to the method described in Section 3.2.3. Two samples were sieved, one which had been extracted to remove the oil and grease from the soil and one which had not been extracted. The results were plotted on logarithmic grain size classification paper. These plots are found in Appendix D-2. The

Table 4.7. Freezing End Point Temperature for Clay

Run #	Sample Top	Middle	Sample Bottom	Freezing Speed
Run 1	-3.04	-3.58	-4.83	Slow
Run 5	-1.78	-0.71	-2.78	Slow
Run 9 & 17	-3.32	-2.76	-4.06	Slow
Run 13 & 21	-2.81	-3.01	-4.06	Slow
Average=	-2.74	-2.52	-3.93	
Standard deviation=	0.67	1.25	0.85	
C.V=	24.53%	49.75%	21.61%	
Run #	Sample Top	Middle	Sample Bottom	Freezing Speed
Run 2	-2.53	fault	-6.5	Fast
Run 6	-3.58	-6.09	-9.7	Fast
Run 10 & 18	-4.63	-5.78	-9.41	Fast
Run 14 & 22	-2.55	-3.78	-7.65	Fast
Average=	-3.32	-5.22	-8.32	
Standard deviation=	1.00	1.25	1.51	
C.V=	30.10%	24.03%	18.18%	

Note: Units are degrees Celsius.
C.V.= coefficient of variation.
The end point temperature is the average freezing temperature maintained in the soil.

Table 4.8. Freezing End Point Temperature for Sand

Run #	Sample Top		Middle		Sample Bottom	Freezing Speed
Run 3	0.57	1.06	0.52	0.65	-0.22	Slow
Run 7	-0.71	-0.99	-2.30	-3.45	-5.34	Slow
Run 11	-1.48	-0.99	-1.53	-1.66	-3.30	Slow
Run 15	-3.78	-3.55	-3.83	-4.22	-5.34	Slow
Run 19	-3.27	-3.30	-3.58	-4.22	-5.60	Slow
Run 23	-3.01	-3.04	-3.58	-3.71	-5.09	Slow
Average=	-1.95	-1.80	-2.38	-2.77	-4.15	
Standard deviation=	1.69	1.81	1.68	1.92	2.10	
C.V=	86.95%	100.34%	70.51%	69.45%	50.55%	
Excluding Run 3:						
Average=	-2.45	-2.37	-2.96	-3.45	-4.93	
Standard deviation=	1.30	1.28	1.00	1.06	0.93	
C.V=	52.92%	53.76%	33.76%	30.58%	18.87%	

Run #	Sample Top		Middle		Sample Bottom	Freezing Speed
Run 4	-0.71	-1.76	-2.81	-4.22	-7.14	Fast
Run 8	data lost	data lost	data lost	data lost	data lost	Fast
Run 12	-1.48	-2.27	-3.58	-5.24	-8.42	Fast
Run 16 & 24	-2.76	-3.50	-4.09	-5.75	-6.88	Fast
Run 20	-2.25	-2.53	-4.09	FAULT	-8.16	Fast
Average=	-1.80	-2.52	-3.64	-5.07	-7.65	
Standard deviation=	0.90	0.73	0.60	0.78	0.75	
C.V=	49.87%	29.03%	16.61%	15.37%	9.84%	

Note: Units are degrees Celsius.

C.V.= coefficient of variation.

The end point temperature is the average freezing temperature maintained in the sc

sandy soil is plotted on Figure D-2.1. and Figure D-2.2. By comparing the two graphs, it is obvious that there is not a large difference between the two soils.

Approximately 85% of the soil particles fall in the sand-size range for both the extracted and non-extracted soil, with the remaining being gravel- and silt-sized. The soil may therefore be roughly characterized as a *slightly silty sand*, meaning a sand with <5% silt (Craig, 1987).

4.2.2. Clayey Soil

The clayey soil was characterized using the hydrometer method outlined in Section 3.2.3. Again, two samples were tested, one being the extracted soil and the other non-extracted. Their grain size distribution curves are found in Appendix D-2, as Figure D-2.3. and Figure D-2.4. The non-extracted soil and extracted soil may both be characterized as *very clayey silt*, that is, a silt with 15-35% clay fraction (Craig, 1987).

The extracted soil was found to contain more clay sized particles (in the order of 40%) than the non-extracted soil (in the order of 25%). This was expected. The non-extracted soil contained oily creosote which binds particles together, and causes them to settle faster than they would if they were not bound by the creosote.

4.3. Raw Results for Aqueous Phase PAH Quantitation

4.3.1. Sandy Soil

Experimental runs were established as described in Section 3.6.1. To reiterate, four run conditions were established, and each run condition was repeated in triplicate for a total of 12 experimental runs. Each run included a total of nine separate batch extractions and chemical analyses of aqueous phase concentrations. Three replicate batch extractions and chemical analyses were performed for each of three soil locations: the unfrozen soil, the frozen soil at the top of the compacted sample, and the frozen soil at the bottom of the compacted sample. Given nine analyses for each of the twelve runs, a total of 108 batch extractions and chemical analyses were performed.

The raw data results of the chemical analysis are located in Appendix A-1. These results are grouped according to experimental conditions. That is, Run 3, 11, and 19 were replicate runs of the same experimental conditions as described in Section 3.6.1. A brief guide to the data contained in Appendix A-1 is located at the beginning of that appendix. Statistical screening information contained with the data is discussed in Section 4.4.1.

4.3.2. Clay Soil

Data was collected for the clay soil in a similar manner to that of the sandy soil. Four experimental conditions were established, and three replicate runs of each set of conditions were performed, making a total of 12 experimental runs. For each run, nine separate batch extractions and chemical analyses of aqueous phase concentrations were performed. Three replicate batch extractions and chemical analyses were performed for each of three soil locations: the unfrozen soil, the frozen soil at the top of the compacted sample, and the frozen soil at the bottom of the compacted sample. Given nine analyses for each of the twelve runs, a total of 108 batch extractions and chemical analyses were performed for the clay.

The raw results from the chemical analysis are in Appendix A-2. A brief guide to the results is located at the beginning of Appendix A-1. Statistical screening information contained with the data is discussed below.

4.4. Raw Data Screening

Raw data may not be used for certain statistical techniques, such as factorial analysis, if it does not satisfy certain criteria. Therefore, the data must be screened. This process is described in the following sections.

4.4.1. Method of Data Screening

4.4.1.1. Statistical Requirements

Data have no meaning in themselves; they become meaningful when related to a conceptual model of the phenomenon studied (Box, Hunter, and Hunter, 1978). Therefore, it is necessary to fit the data obtained to a model. One means of fitting data to a model is through the use of a statistical factorial analysis of data. However, the use of factorial analysis assumes that certain conditions of the data are met. These include: the data are randomly distributed, genuine run replicates are conducted, the data is statistically independent, and the data follows approximately a normal distribution (Box, Hunter and Hunter, 1978).

The data are randomly distributed, since runs were conducted in a random order. Genuine run replicates were performed, as each sample started with fresh soil and cleaned equipment. The data is statistically independent as each value is measured independently of a previous value. A check for normally distributed data is required, and is discussed below.

4.4.1.2. Normality

A simple check for normality is to plot the data to determine if it follows approximately a normal curve. Figure 4.1. shows a normal curve, as well as the plot of an actual sample data set. It is obvious from the graph that the sample data set does not follow the normal curve very well. However, this data set simply appears to be skewed upwards from the normal curve. This implies that a transformation of the data may better fit the data to an approximate normal curve.

One data transformation is a logarithmic transformation. This is shown in Figure 4.2. with an approximate normal curve. By transforming the data to a logarithmic distribution, the data appears to follow more closely a normal distribution.

Figure 4.1. Normally Distributed Data vs. Actual Sample Data

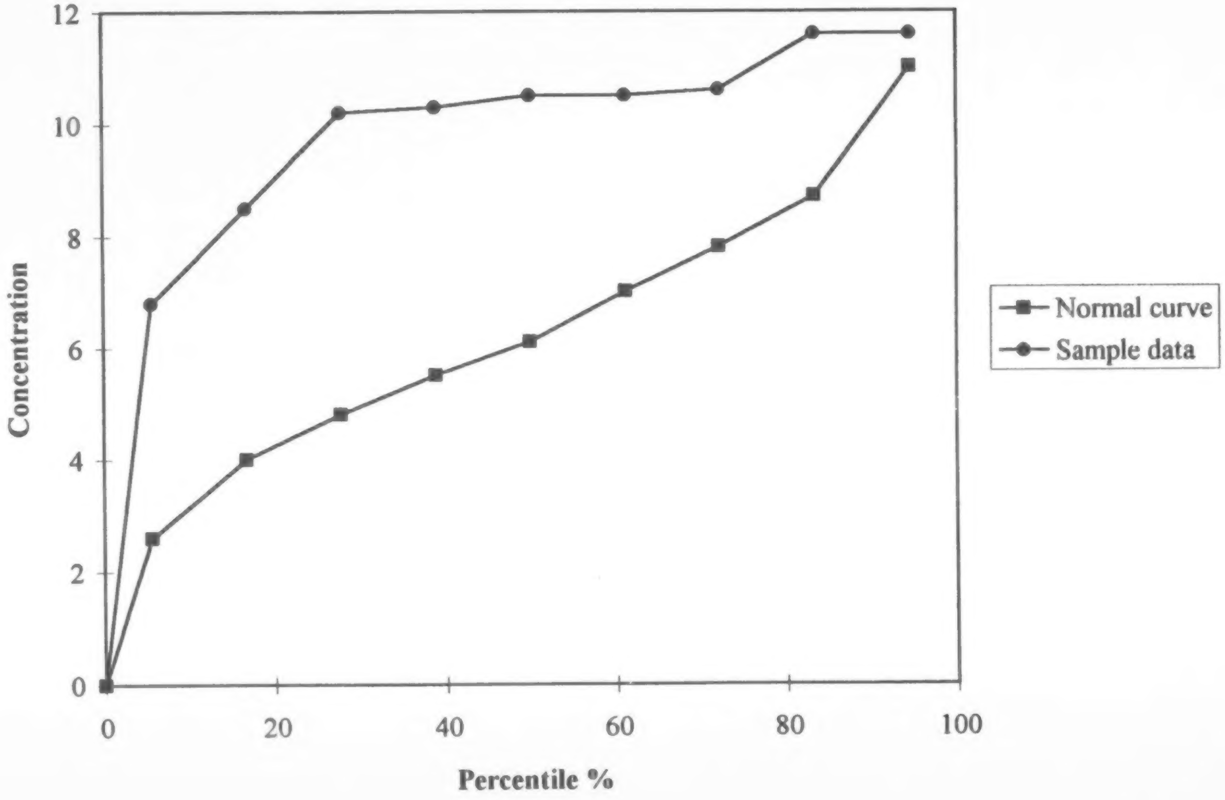
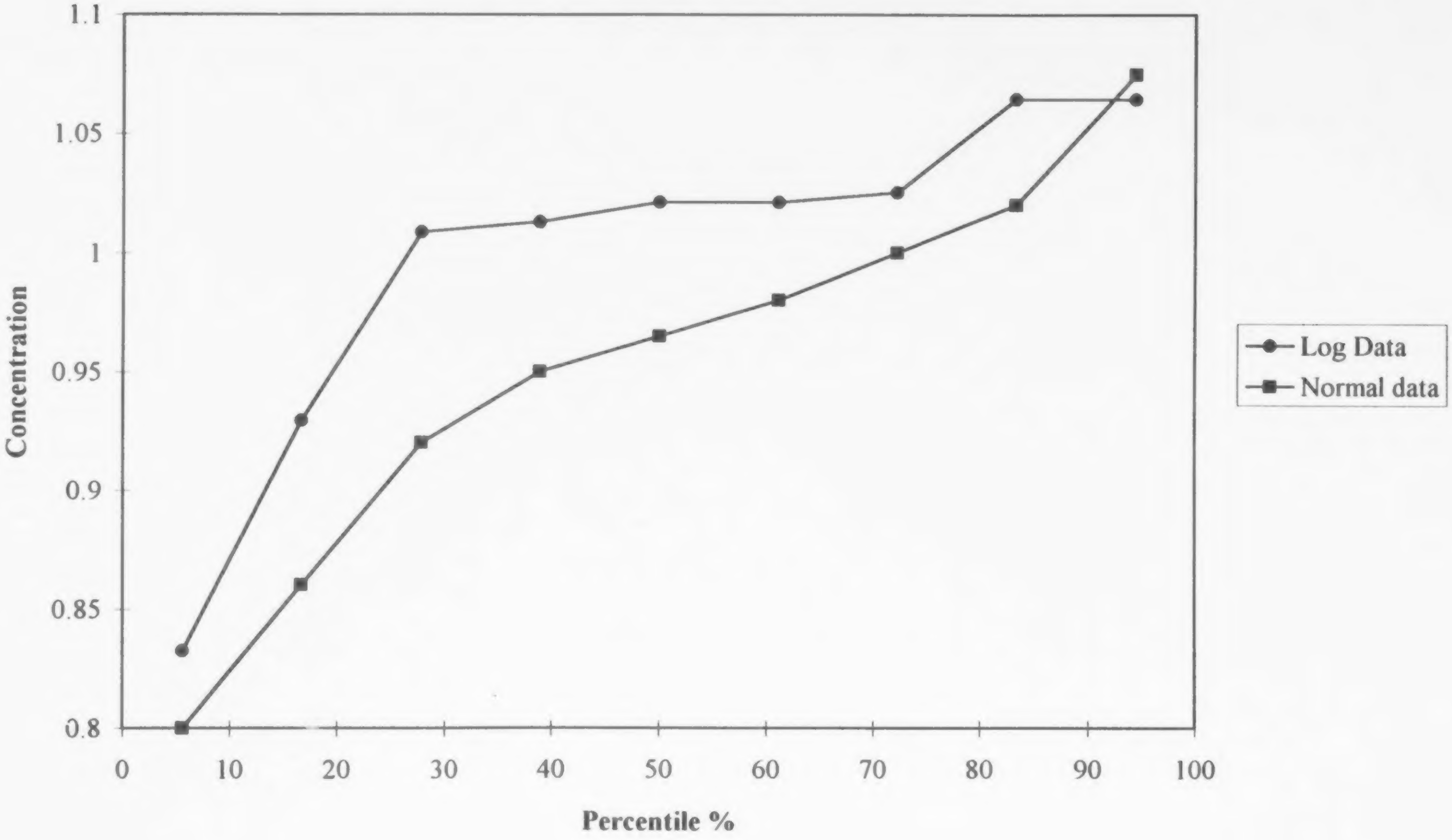


Figure 4.2. Log Transformed Data vs. Normal Data Plot



The data was first analyzed using the raw data values, not transformed values. By running a simple comparison test, this may be justified. That is, if reanalyzing the most significant results using the logarithm values gives the same results as for the untransformed raw data values, then using the untransformed values for analysis is acceptable.

This was done for all the factorial calculations where significant effects were found, and the logarithmic values produced the same levels of significance as the untransformed values. Therefore, it was acceptable to use the untransformed data values for all the statistical analyses. The logarithmic factorial calculations are located in Appendix B-1 for clay and Appendix B-2 for sand, and follow the appropriate factorial calculation sheet of the raw data.

4.4.1.3. Tests for Outlying Data Points

Several tests for outlying data exist. One check is that any data that lies more than three standard deviations from the mean should be discarded (Byrkit, 1987). However, when dealing with small sets (n<10) of analytically obtained data, statistical methods applicable to large data sets become less useful, may be more difficult to interpret, and may even become misleading (Knettig, 1994). Specific techniques have been developed for cases involving smaller data sets.

One such technique for data points is called the "Q-test". It uses the following equation:

$$Q_{obs} = \left| \frac{\text{suspect value - nearest value}}{\text{largest value - smallest value}} \right|$$

where "nearest value" refers to the value numerically closest to the suspect value, and largest and smallest are respectively the largest and smallest values in the data set. Q_{obs} represents the observed Q value, and is then compared to a standard tabulated value based on data set size. This technique was not used because it was not easily adaptable to a computer spreadsheet.

The second criterion for rejection of outlying data for small data sets is called "Chauvignot's Criterion". An observation in a sample size of n samples is rejected if it deviates from the mean more than a value corresponding to $(1/2n)\times$probability. The probability is calculated on the assumption of a normal distribution, with the variance calculated from the data in the sample set (Knettig, 1994). The boundaries of the criteria follow:

$$\text{Mean} - (\text{probability}\times\text{variance}) < \text{DATA POINT} < \text{Mean} + (\text{probability}\times\text{variance})$$

Values which lie outside the limits established by the criterion are considered "outliers" and may be considered for rejection.

Chauvignot's Criterion was used as the main data rejection criteria. Any data points which were outliers by Chauvignot's criterion were considered for rejection.

Values that lay outside the criterion range by ±0.02 ug/g were accepted for use and are marked in the data tables enclosed by a box. Any values exceeding this were tested for normality by graphing the data set as a probability plot, and comparing the curve to an approximate normal distribution. If the point lay roughly on the normal distribution, it was accepted. Using this technique, data was tested twice to ensure points which appeared to be outliers were indeed bad data points.

4.4.2. Results of Data Screening Process

4.4.2.1. Clay Soil

For the clay soil, there were relatively few outliers. Naphthalene was frequently an outlying value, however, this is expected due to its high volatility. Simply overdrying a sample can significantly reduce the naphthalene concentrations, as can leaving the sample exposed to air for prolonged periods of time. Because it was difficult to know if a sample had been overdried or if excessive losses to the atmosphere had occurred, values of naphthalene which were outliers by Chauvignot's Criteria were accepted as valid data.

Soil in general is heterogeneous in nature. The distribution of contamination in soil is particularly heterogeneous, varying from one point in the soil matrix to the next (McGill, 1980). The heterogeneity of the actual subsurface environment must be recognized (Hrudey and Pollard, 1993). Given this heterogeneity, it likely that the standard deviations of any data for soil will be high. For this reason, unless a data value was an obvious error, data was generally accepted.

As stated in Section 4.4.1, for all outlying points, plots of the data set were made to determine if the data fell on a normal curve. In every case, it was found that the outlier fell reasonably well on the normal distribution curve. Therefore, none of the collected data was discarded for the clay soil.

Returning briefly to the example of Figure 4.1., it was found that all the data for that sample data set fell well within Chauvignot's Criterion. By graphing the data only, interpretation is difficult and highly subjective. By using first Chauvignot's criteria and then the comparison of the data plot to an approximate normal curve as a second check, the amount of data collected which was used for statistical analysis was maximized.

4.4.2.2. Sandy Soil

The data for the sandy soil was subjected to the same treatment as the clay soil. Again, by using both criteria, the amount of useful collected data was maximized. No data points were discarded for the sandy soil.

4.5. Method of Hypothesis Testing

4.5.1. Factorial Analysis and ANOVA

Once the data was screened, it was deemed acceptable for use in statistical analysis. The hypotheses (as in Section 2.4.) to be tested are:

(1) freezing and thawing of a creosote contaminated soil will increase the availability of the creosote to the aqueous phase;

(2) location of sampling following freezing may be a significant factor affecting the availability of PAHs to the aqueous phase (i.e. movement of PAHs may be significant);

(3) freezing with a high soil moisture content will have a significantly greater effect than freezing with a low moisture content in terms of causing increased PAH availability following freezing;

and

(4) a fast freezing rate will be significantly more effective than a slow freezing rate to cause increased availability of PAHs following freezing.

In order to test the hypotheses, one factorial analysis and one analysis of variance (ANOVA) were used. The factorial analysis was a 2^3 factorial, where three effects were examined at two levels each. The effects studied included the effects of moisture content, the effect of freezing rate, and the effect of sampling location on the amount of PAHs available to the aqueous phase following freezing. The two levels of moisture content were the in-situ and near field capacity values. The two levels of freezing rate were a "fast" and a "slow" setting. The two levels for PAH sampling location were the top of the soil sample and the bottom of the sample. The factorial analysis tested Hypotheses 2, 3, and 4. As well, a benefit of using factorial analysis was the identification of significant interactions between factors. The arrangement of the data for the factorial analysis is shown in Table 4.9.

Table 4.9. Factorial Analysis

Moisture Level	Location	Freezing Rate
Low	Bottom	Slow
High	Bottom	Slow
Low	Top	Slow
High	Top	Slow
Low	Bottom	Fast
High	Bottom	Fast
Low	Top	Fast
High	Top	Fast

The factorial analysis was performed for each individual PAH data set with significantly high concentrations, as well as for the data set containing the sum, or total, concentration of the 16 Priority PAHs detected. A brief review of the raw data showed that several of the 16 Priority PAH compounds had very low aqueous phase concentrations, and some were non-detectable. Compounds such as indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene were frequently found to exist in aqueous phase at non-detectable levels, which is expected given the very low aqueous solubilities for those compounds. Also, for some compounds, the standard deviation of the data set was greater than 50% of the average mass of PAH being measured. For these data sets, there was too much variability in the data to produce any meaningful conclusions regarding trends in the data. Therefore, these data sets were not analyzed statistically.

The analysis of variance (ANOVA) was used to test Hypothesis 1, the significance of freezing. Since the factorial analysis was performed first, data from different experimental conditions which were found to be insignificant were grouped together for the ANOVA. The ANOVA was a classical one-way ANOVA, where data from before freezing were compared to data after freezing to determine if significant differences existed. The method is discussed in detail in section 4.5.3. Similar to the factorial analysis, only certain PAH data sets were analyzed for the ANOVA and the criteria for which sets were analyzed was the same as for the factorial analysis.

4.5.2. Factorial Calculations

The calculations to determine the magnitude of the effects of variables on PAH concentrations were performed using Yates Algorithm as described in Box, Hunter and Hunter (1978), Montgomery (1984), and Walpole and Myers (1987). A sample data sheet of the calculations is found in Table 4.10.

Yates algorithm organizes the data into Standard Order, and then sums the totals across the rows of data. A series of operations is then performed on the data. The Sum

Table 4.10. Sample Factorial Calculations Data Sheet

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture content	Location	Freezing Rate	Replicate 1	Replicate 2	Replicate 3	Totals	(1)	(2)	(3)	Sum of Squares	Degrees of Freedom	Mean Square	Effects
low	bottom	slow	90.89	86.95	75.00	252.8	521.46	1036.74	***2084.08***				
high	bottom	slow	81.20	93.68	93.74	268.6	515.29	1047.34	121.30	613.03	1	613.03	10.108
low	top	slow	75.27	76.87	79.54	231.7	522.81	67.71	-4.46	0.83	1	0.83	-0.371
high	top	slow	83.23	90.81	109.57	283.6	524.53	53.59	67.67	190.81	1	190.81	5.639
low	bottom	fast	85.28	83.41	87.20	255.9	15.77	-6.17	10.60	4.68	1	4.68	0.883
high	bottom	fast	83.65	96.84	86.44	266.9	51.94	1.71	-14.12	8.31	1	8.31	-1.177
low	top	fast	76.57	81.17	83.25	241.0	11.04	36.17	7.88	2.59	1	2.59	0.657
high	top	fast	82.44	100.90	100.19	283.5	42.55	31.50	-4.66	0.91	1	0.91	-0.389
				Total sum of data=		***2084.1***			**Sum=**	**821.15**			
				Sum of squares of data=		182760.4			**Error=**	**964.27**	16	60.27	
								Sum of Squares total=		**1785.43**			
			Check:	**(1)**	**(2)**	**(3)**							
			545388	**1090777**	**2181554**	**4363108**							

of Squares for each row is obtained by squaring the appropriate value in column (3) and dividing by the total number of data points in the set (i.e. 72). The effects are calculated from Column (3) divided by one half of the total number of data points in the set. The effects may then be plotted on normal probability paper. Effects laying along a straight line are considered insignificant, and effects which deviate from the straight line are considered significant (Box, Hunter, and Hunter , 1978).

A second less subjective test to determine the significance of effects is done through an Analysis of Variance (ANOVA) table, in which the F statistic is calculated for each effect, and compared to a tabulated F level of significance. Any calculated F which exceeds the tabulated value indicates a significant effect. A sample of these calculations are found in Table 4.11. The F statistics are calculated from the Sum of Squares column. The "Total Sum of Squares" is the sum of the "Sum of Squares" column. The error term, or sum of squares error, is derived by subtracting the individual sum of squares for each effect from the "Total Sum of Squares". The Mean Square is derived by dividing the sum of squares for each row by the degrees of freedom for that row. Finally, the calculated F is derived by dividing the Mean Square value by the Mean Square for the Error term. The tabulated F is obtained from statistical F distribution tables found in a statistics book for the value F*(degrees of freedom of effect, degrees of freedom of error)* (Box, Hunter and Hunter, 1978; Montgomery, 1984; and Walpole and Myers, 1989).

The calculations and results of the calculations are organized in Appendix B-1 for the factorial analysis for the clay soil and Appendix B-2 for the sandy soil.

The method used to determine the validity of the significant effects was a reverse-Yates Algorithm. This technique determines the "predicted" values based on a model employing only significant effects. These "predicted" values are then subtracted from the actual experimental values, and each difference or "residual" is plotted. The model is valid if the residuals follow approximately a normal curve. This ensures the validity of the calculated effects. A sample calculation is shown in Table 4.12.

The check for the validity of the significant effects are included in Appendix B-1 for acenaphthene in clay and for the sum PAH data for clay. For brevity, the calculations are not included for other PAH data. For acenaphthene and the sum PAH data for clay,

Table 4.11. Sample Analysis of Variance Calculation Data Sheet

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	Calculated F	Significant?
a=moisture	613.03	1	613.03	10.17	yes-99%
b=location	0.83	1	0.83	0.01	no
ab	190.81	1	190.81	3.17	no
c=fr.rate	4.68	1	4.68	0.08	no
ac	8.31	1	8.31	0.14	no
bc	2.59	1	2.59	0.04	no
abc	0.91	1	0.91	0.02	no
Error	964.27	16	60.27		

Tabulated F values:
f -95% (1,16)=4.49
f -99% (1,16)=8.53

Table 4.12. Sample Residuals Calculation Data Sheet Using Reverse Yates Algorithm

						Predicted y				Residuals=actual - predicted		
	Effects	(1)	(2)	(3)	Divisor	y^	Actual y Values			y-y^		
abc	0.00	0.00	0.00	***2099.52***	24	87.48	90.89	86.95	75.00	3.41	-0.53	-12.48
bc	0.00	0.00	2094.23	2068.64	24	86.19	81.20	93.68	93.74	-5.00	7.48	7.54
ac	0.00	5.29	0.00	2088.93	24	87.04	75.27	76.87	79.54	-11.77	-10.17	-7.50
c=rate	0.00	2094.23	2068.64	2079.23	24	86.63	83.23	90.81	109.57	-3.40	4.18	22.94
ab	5.29	0.00	0.00	2099.52	24	87.48	85.30	83.41	87.20	-2.18	-4.07	-0.28
b=location	0.00	0.00	2088.93	2068.64	24	86.19	83.65	96.84	86.44	-2.54	10.64	0.25
a=freezing	10.14	-5.29	0.00	2088.93	24	87.04	76.57	81.17	83.25	-10.47	-5.87	-3.79
average	2084.08	2073.94	2079.23	2079.23	24	86.63	82.44	100.90	100.19	-4.19	14.27	13.56
Sum=	***2099.52***											
	Sums of squares check:											
	4343531	8687062	17351921	34748246								
	Effects	(1)	(2)	(3)								

the residuals followed a normal distribution which indicates the effects which were calculated to be significant were verified as significant (Box, Hunter and Hunter, 1978).

A second check on the calculations in Yates algorithm is that the sums of squares of the "TOTALS" column should be equal to 0.5×Column (1), and equal to 0.25×Column(2), and equal to 0.125×Column (3) (Box, Hunter and Hunter, 1978). This check was performed for each calculation and the check was valid for every case. This calculation is shown at the bottom of Table 4.10. and also Table 4.12.

4.5.3. ANOVA Calculations

The calculations to determine if freezing was a significant factor in increasing the aqueous availability of PAHs followed a one-way analysis of variance (ANOVA). As the calculations are arithmetically simple, they are not shown explicitly here in a table but are found in Appendix C-1 for clay and Appendix C-2 for sand. A brief introduction to the layout of the data is given at the beginning of Appendix C-1.

For this technique, the "before freezing" data was grouped and the "after freezing" data was grouped. The sum of all the values in each group was calculated. Using these sums, the sum of squares for the between-treatments variation was calculated as well as the total sum of squares. The error variation, or variation between replicated runs, was calculated by subtracting the between-treatments sums of squares from the total sums of squares. The mean squares for between-treatments and for between-replicates were calculated by dividing the respective sums of squares by the degrees of freedom for that source of variation. The F statistic was calculated by dividing the between-treatments mean square by the between-replicates mean square. The calculated F statistic was compared to a tabulated F statistic based on the degrees of freedom of between-treatments and the total degrees of freedom (Walpole and Myers, 1989 and Montgomery, 1984).

A check on these calculations was done for random samples by using the Excel 5.0 built-in statistical ANOVA analysis function.

4.5.4. Sandy Soil Data Sets

Data sets which were considered to be unsuitable for analysis had a statistical standard deviation which was larger than half of any value within that data set. For these sets, there was too much inherent variability within the data which would mask any effects. Therefore, only data which had a standard deviation smaller than half of any value within the data set was analyzed. For sand, the PAH compounds which contained suitable PAH concentration data for analysis were:

-Total PAHs
-Phenanthrene
-Fluorene
-Naphthalene
-Fluoranthene
-Benzo (b+k)pyrene
-Acenaphthene
-Pyrene

The factorial analysis for these compounds for the sand soil are in Appendix B-2, and the ANOVA calculations for these compounds are in Appendix C-2.

4.5.5. Clay Soil Data Sets

The criteria for acceptable data for clay was identical to the criteria for the sandy soil. Data sets which were considered to be unsuitable for analysis had a statistical standard deviation which was larger than half of any value within that data set. Therefore, for the clay soil, the data sets which were analyzed included:

-Total PAHs
-Phenanthrene
-Fluorene
-Fluoranthene
-Acenaphthene
-Pyrene

The factorial data for these compounds for the sand soil are in Appendix B-1, and the ANOVA calculations for these compounds are in Appendix C-1.

4.6. Quality Assessment and Quality Control Results

4.6.1. Accuracy Results

As stated in Section 3.5.1., the method of accuracy testing had two components.

4.6.1.1. Accuracy for PAH Oil Phase Quantitation

The determination of accuracy for the TPHC level determination was carried out through the use of certified reference standard materials. The materials obtained were two Marine Sediments from the National Research Council of Canada Sediment Standards Division. One sediment, labelled Soil HS-3, was obtained from a highly contaminated area, and the other, labeled Soil HS-6, was from a slightly contaminated area.

The standards were used for several checks for accuracy. As the Standard Sediments were relatively free of interfering compounds, a clean-up process was not absolutely required to obtain good quality PAH concentration data. Efficiency of the following procedures were tested by comparing PAH concentration data obtained to the standard values.

1. The efficiency of the Soxhlet extraction was determined by running the sediment through a Soxhlet extraction.
2. The efficiency of the Florisil clean-up was checked by Soxhlet extraction of the sediment followed by the Florisil column chromatography clean-up step only. The eluate was collected after nitrogen blowdown.
3. Efficiency of the total clean-up was determined by Soxhlet extraction, followed by the Florisil and alumina column chromatography clean-up steps. The eluate was collected after rotary evaporation.

In all cases, the extract or eluate collected was then subjected to GC/MS analysis for quantitation of the 16 PAHs of interest.

The results of the efficiency testing are found in Table 4.13. The results are listed according to the treatment applied to the sediment. The acceptable range data was

Table 4.13. Accuracy Check for Soxhlet Extractions
and Clean-Up Steps

Compound	Acceptable Range µg/g	**Soxhlet only µg/g**	Error	**Florisil only µg/g**	Error	**Full treatment µg/g**	Error
Naphthalene	8.3-9.7	**7.24**	-12.8%	**7.26**	-12.5%	**6.69**	-19.4%
Acenaphthalene	0.2-0.4	**0.5**	25.0%	**0.45**	12.5%	**0.35**	in range
Acenaphthene	3.0-6.0	**3.22**	in range	**3.3**	in range	**2.98**	-0.7%
Fluorene	10.2-16.4	**7.51**	-26.4%	**7.96**	-22.0%	**8.04**	-21.2%
Phenanthrene	65-105	**73.67**	in range	**73.62**	in range	**76.29**	in range
Anthracene	12.9-13.9	**0**	100.0%	**3.96**	-69.3%	**9.05**	-29.8%
Fluoranthene	51-69	**87.18**	26.3%	**70.01**	1.6%	**63.27**	in range
Pyrene	30.0-48.0	**23.83**	-20.6%	**21.01**	-30.0%	**21.37**	-28.8%
Benz(a)anthracene	12.6-16.6	**8.51**	-32.5%	**11.34**	-10.0%	**11.21**	-11.0%
Chrysene	12.1-16.1	**15.47**	in range	**10.52**	-13.1%	**9.99**	-17.4%
Benzo(b+k)fluoranthene	8.3-14.7	**11.13**	in range	**10.99**	in range	**12.23**	in range
Benzo(a)pyrene	3.8-11.0	**4.16**	in range	**4.3**	in range	**5.56**	in range
Indeno(1,2,3-cd)pyrene	4.1-6.7	**3.08**	-24.9%	**3.34**	-18.5%	**4.53**	in range
Dibenz(a,h)anthracene	.8-1.8	**0.24**	-70.0%	**0.51**	-36.3%	**1.8**	in range
Benzo(g,h,i)perylene	3.0-7.0	**3.44**	in range	**3.41**	in range	**4.68**	in range

supplied by the National Research Council of Canada, who exhaustively quantitated the 16 PAH compounds in the samples. Thorough homogenization of the samples had been performed by the NRC, and the range of concentrations established by the NRC is accurate to the 99th percentile.

Errors for the "Soxhlet only" ranged from 12.8% for naphthalene to 70% for dibenz(a,h)anthracene and 100% for anthracene. The large error associated with anthracene is due to its incorrect peak integration by the MS Chemstation software. This is because the chromatographic peak for phenanthrene is integrated in the same window as anthracene. Phenanthrene however has a very large chromatographic peak compared to the peak size for anthracene. Therefore, the peak for anthracene was frequently overlooked and integrated as zero. Manual integration of the anthracene peak proved tedious and did not yield consistent results.

The large error for dibenz(a,h)anthracene is expected since this compound had a very low concentration (0.8-1.8 μg) in the sediment standards. This level of concentration was below the detection limits for this analysis.

For the Florisil treatment, the errors were approximately ±20% for the compounds of interest. Accuracy for the heavier compounds (benz(a)anthracene and below) was not important because these compounds showed too much variability and were not analyzed statistically. The high error associated with anthracene exists for the reasons indicated in the previous section (improper peak integration).

The full treatment (Soxhlet, Fluorisil and alumina clean-up) surprisingly yielded the best results of the three treatments. Of the 16 PAHs, 8 fell in the correct range and the others were not out by extremely large amounts. Compounds of interest varied by a maximum of 29% from the Standard determined value.

4.6.1.2. Accuracy for PAH Aqueous Phase Quantitation

The method of measuring accuracy for the aqueous phase determinations was described in detail in Section 3.5.1. Performance evaluation samples were run. In this process, Sandra Kenefick, the Laboratory Chemist, added known quantities of PAHs to five batch equilibrium bottles which had been pre-prepared. Then, the bottles were subjected to tumbling for 24 hours for equilibration, followed by the same procedures as other samples for aqueous phase PAH determinations.

The GC/MS data obtained for these samples was then compared to the concentration values which were known added concentrations by Ms. Kenefick. This data is presented in Table 4.14. on the following page.

For Sample 1, the error ranged from 5% for fluorene to 90% for indeno(1,2,3-c,d)pyrene. The errors were all fairly low for the PAHs of interest which were accepted for statistical analysis. The only two accepted compounds which had high errors were phenanthrene (20% error) and pyrene (60%).

For Sample 2, the error ranged from 5% for fluorene to 99.8% for benzo(g,h,i)perylene. Again, the accepted PAH compounds had fairly low error, except for acenaphthalene and pyrene.

For Sample 3, errors for the accepted PAHs were low except for pyrene with an error of 67%.

The data for Sample 4 and 5 is not presented. This is because for Sample 4 and Sample 5, the errors were very high because of low concentrations of PAHs added to the aqueous phase for these samples. It was determined that using these methods and procedures, the detection limit of the GC/MS equipment was approximately 1 μg. This means any quantity existing below a concentration of 1 μg may not be reported as accurate and there is a high degree of uncertainty associated with that value.

4.6.2. Precision

As stated in Section 3.5.2., precision is a measure of the degree of closeness by which multiple analyses of a given sample agree with each other, and is generally reported as the standard deviation of the results (APHA, AWWA, WEF, 1992). A point to note before analyzing precision however, is that soil is by nature an extremely heterogeneous medium (McGill, 1980; Hrudey and Pollard, 1993). It is expected that standard deviations would be fairly high.

Table 4.14. Accuracy Results for Aqueous Phase Extractions

	Sample 1			Sample 2			Sample 3		
Compound	Expected Value µg/g	Obtained Value µg/g	Error %	Expected Value µg/g	Obtained Value µg/g	Error %	Expected Value µg/g	Obtained Value µg/g	Error %
Naphthalene	10	8.7	-13.0	20	16.2	-19.0	15.0	11.9	-20.7
Acenaphthalene	20	16.9	-15.5	40	24.6	-38.5	30.0	23.8	-20.7
Acenaphthene	10	9.4	-6.0	20	18.6	-7.0	15.0	13.1	-12.7
Fluorene	2	1.9	-5.0	4	3.8	-5.0	3.0	2.6	-13.3
Phenanthrene	1	1.2	20.0	2	2	in range	1.5	1.4	-6.7
Anthracene	1	0.6	-40.0	2	1.1	-45.0	1.5	0.7	-53.3
Fluoranthene	2	2	in range	4	3.3	-17.5	3.0	2	-33.3
Pyrene	1	0.4	-60.0	2	0.7	-65.0	1.5	0.5	-66.7
Benz(a)anthracene	1	0.5	-50.0	2	0.2	-90.0	1.5	0.3	-80.0
Chrysene	1	0.2	-80.0	2	0.3	-85.0	1.5	0.2	-86.7
Benzo(b+k)fluoranthene	3	0.6	-80.0	6	0.5	-91.7	4.5	0.7	-84.4
Benzo(a)pyrene	1	0.3	-70.0	2	0.1	-95.0	1.5	0.1	-93.3
Indeno(1,2,3-cd)pyrene	1	0.1	-90.0	2	n/d	100.0	1.5	0.04	-97.3
Dibenz(a,h)anthracene	2	0.3	-85.0	4	n/d	100.0	3.0	0.1	-96.7
Benzo(g,h,i)perylene	2	0.4	-80.0	4	0.01	-99.8	3.0	0.1	-96.7
Totals	58	43.5	-25.0	116	71.41	-38.4	87	57.54	-33.9

Standard deviations were calculated for the set of data which describes aqueous availability for one set of run conditions. That is, a low moisture content and fast freezing rate for clay soil at the top of the sample after freezing is one set of run conditions. A total of nine data points should exist for each set, as three frozen and thawed samples were prepared, and from each of the three, a total of three analyses were performed giving the total of nine values in the data set.

The complete analysis of standard deviations is found in Appendix E-1, along with a brief introduction to the data. As the data are fairly numerous, they are not included here. However, Table 4.15. provides a summary. From this table, it is obvious that naphthalene had a high coefficient of variation (coefficient of variation equals the standard deviation divided by the mean) both for clay and sand. The coefficient of variation (C.V.) gives an indication of the amount of variability, or error, that exists for an average set of nine data points. A high C.V. for naphthalene is expected because of its relatively high volatility. Heating the sample too much or exposing the sample to the atmosphere for a prolonged time eliminates much of the naphthalene that was present.

The C.V. for acenaphthalene, acenaphthene, fluorene, and phenanthrene was, for the most part, below 20%. The C.V. for fluoranthene was above 30% for the sand, but below 20% for the clay. This indicates poor reproducibility for analysis of fluoranthene for the sand. This could be due to the MS Chemstation software technique for peak integration. Fluoranthene and pyrene were both integrated in the same window of retention time. However, if one chromatographic peak was much larger than the other, the smaller peak was frequently overlooked or integrated as zero. This poor integration was inconsistent, and did not always occur thus causing high variability for the concentration of fluoranthene.

Pyrene had a fairly low C.V., approximately 20%. Benz(a)anthracene had a very high C.V., particularly for the clay soil. This is likely due to improper integration, the same problem that occurred for anthracene and fluoranthene. The chromatography during the running of some clay samples was poor, and the peak for benz(a)anthracene occasionally did not even appear on the chromatogram. This explains the highly variable data values obtained for benz(a)anthracene.

Table 4.15. Summary of Precision Results for Clay and Sand

	CLAY				SAND			
Conditions->	Low moisture	Low moisture	High moisture	High moisture	Low moisture	Low moisture	High moisture	High moisture
Conditions->	Slow freezing	Fast freezing	Slow freezing	Fast freezing	Slow freezing	Fast freezing	Slow freezing	Fast freezing
Compound	Runs 1,9,17 **Coefficient of variation %**	Runs 2,10,18 **Coefficient of variation %**	Runs 5,13,21 **Coefficient of variation %**	Runs 6,14,22 **Coefficient of variation %**	Runs 3,11,19 **Coefficient of variation %**	Runs 4,12,20 **Coefficient of variation %**	Runs 7,15,23 **Coefficient of variation %**	Runs 8,16,24 **Coefficient of variation**
Naphthalene	35.7	45.6	40.4	35.0	24.9	53.6	40.5	28.8
Acenaphthalene	24.7	21.8	12.4	24.1	45.8	30.3	15.9	11.0
Acenaphthene	10.9	7.2	7.1	6.8	15.0	17.8	13.9	8.1
Fluorene	5.9	5.0	6.8	8.4	15.7	19.7	14.4	9.7
Phenanthrene	10.9	11.6	13.6	9.2	12.5	23.7	22.0	15.2
Fluoranthene	19.1	17.5	16.4	14.6	34.9	37.0	34.9	34.4
Pyrene	11.5	14.3	22.2	20.3	26.9	46.5	31.9	22.2
Benz(a)anthracene	120.8	75.7	129.7	71.9	29.1	52.5	9.7	4.0
Chrysene	26.3	29.3	46.7	62.3	25.4	56.6	31.7	30.8
Benzo(b)pyrene	35.7	51.5	46.1	56.7	25.6	48.4	40.7	34.2
Benzo(k)pyrene	26.3	50.3	46.3	23.8	33.2	74.3	36.9	19.8
Benzo(a)pyrene	124.7	79.4	nd	nd	nd	56.5	43.3	35.9

Chrysene also had high C.V., averaging approximately 40% for clay and 35% for sand. This could be due also to the fact that chrysene is integrated in the same window as benz(a)anthracene, and frequently these two compounds produced poor chromatographic results. The peaks for these compounds appear very close together on the chromatogram, having retention times separated by a maximum of 0.1 minutes. Frequently, a rather broad single peak appeared for the benz(a)anthracene and chrysene while other times, two distinct peaks were visible and integrated. Data for chrysene was not analyzed statistically due to its high variability and poor chromatography.

The C.V.'s for benzo(b)pyrene, benzo(k)pyrene, and benzo(a)pyrene were all very high. This was likely due to their low aqueous solubilities and subsequent low concentrations in the aqueous phase. In many cases, these compounds were non-detectable. In other cases, the chromatography for the peaks was very poor, particularly for benzo(b)pyrene and benzo(k)pyrene, since their retention times differ by only 0.08 minutes. A single broad peak frequently appeared for these compounds, and was integrated incorrectly. Therefore, no statistical analysis was attempted for any of the compounds with molecular masses greater than benz(a)anthracene and chrysene (molecular mass 228). This was due to the poor chromatography and peak resolution, and resulting high C.V. associated with these compounds.

4.6.3. Sample Recovery

As a check for sample recovery, an internal standard of deuterated anthracene was added to each sample, just prior to injection of the sample into the GC. It was assumed that the anthracene standard added was of a known concentration and known volume, therefore a known mass. By comparing the mass of the anthracene standard recovered to the mass of the other five deuterated surrogate standards recovered, the approximate recovery of the sample was known.

While this method appears logical, there were several limitations. First, the mass spectrometer response for the surrogate standards required response correction factors applied to the peak areas of the surrogate standards obtained. These response factors are calculated by injecting a known amount of anthracene standard and a known amount of the five surrogate standards, related by various ratios depending on the amounts added. If an identical quantity of each is injected, the ratio is one. When comparing the areas of the resulting chromatographic peaks, the areas should be the same since the masses injected were identical. However, this was not the case for this instrument and therefore, a correction factor was required to correct the area of the peaks of the surrogate standards so that the peak areas of the internal standard and surrogate standard correspond to each other.

An ideal situation occurs when the response of the mass spectrometer is linear. That is, for any ratio of mass of internal standard to mass of surrogate standard, the response factor will always be the same (the ratio of the areas of the peaks will always be the same). However, the response was not linear with the mass spectrometer used for this analysis. The ratios of the peak areas varied depending on the masses of the standards used. To compensate for this, the best approximation was to use average values for the response factors obtained. The factors determined as well as the average values are in Table 4.16.

By using these response factors and calculating the amounts of surrogate standard recovered, the amount of deuterated naphthalene recovered was consistently smaller than for the other compounds. Recoveries ranged from 50-80% for naphthalene. Phenanthrene recovery was generally acceptable, ranging from 70-100%. Recovery for deuterated chrysene and deuterated perylene were high. Recoveries ranged from 100-130%. One possible explanation for recovery above 100% involves the evaporation of solvent from the standard mixes. The five deuterated standards dissolved in dichloromethane (DCM) solvent were kept for several months in 7mL vials. When a volume of the standard mix was removed from the vial, the gaseous headspace in the vial increased. Because DCM is extremely volatile, some solvent evaporated into the headspace. So for a given mass of standards, the volume of the solvent containing those standards is decreased. The standards are thus concentrated in the solvent. When a volume of the standard mix is removed and the concentration of standards in that volume is assumed, the assumption is incorrect. The concentration of standards in the solvent is

Table. 4.16. Anthracene Internal Standard Response Factor Ratios

Ratio	**Deuterated Standard**	**Response Factor**	**Response Factor**	**Response Factor**	**Average Factor**	**Standard Deviation**
6	136	0.774	0.752	0.919	**0.815**	0.09
6	164	1.401	1.281	1.602	**1.428**	0.16
6	188	0.748	0.659	0.836	**0.748**	0.09
6	240	0.631	0.511	0.703	**0.615**	0.10
6	264	0.850	0.630	0.931	**0.804**	0.16
4	136	0.808	0.714	0.659	**0.727**	0.08
4	164	1.778	1.517	1.652	**1.649**	0.13
4	188	0.831	0.683	0.740	**0.751**	0.07
4	240	0.889	0.813	0.831	**0.844**	0.04
4	264	0.860	0.827	0.817	**0.834**	0.02
3	136	0.977	0.927	0.834	**0.913**	0.07
3	164	1.710	1.640	1.503	**1.617**	0.11
3	188	0.918	0.886	0.796	**0.866**	0.06
3	240	0.810	0.787	0.687	**0.761**	0.07
3	264	1.121	1.105	0.951	**1.059**	0.09
2	136	0.838	0.819	0.768	**0.808**	0.04
2	164	1.468	1.421	1.401	**1.430**	0.03
2	188	0.792	0.775	0.768	**0.778**	0.01
2	240	0.692	0.674	0.660	**0.676**	0.02
2	264	0.871	0.973	0.946	**0.930**	0.05

Note: the numbers under the deuterated standard column denote the atomic mass of the deuterated standard added. 136=naphthalene; 164=acenaphthalene; 188=phenanthrene; 240=chrysene; and 264=perylene.

	Summary of averages of average factors				
Ratio	136	164	188	240	264
6	0.815	1.428	0.748	0.615	0.804
4	0.727	1.649	0.751	0.844	0.834
3	0.913	1.617	0.866	0.761	1.059
2	0.808	1.430	1.430	0.676	0.930
Averages	0.861	1.524	1.148	0.719	0.995

no longer known because the solvent volume has changed an unknown amount as a result of solvent evaporation. The real concentration is greater than the assumed concentration.

Another cause for recovery above 100% relates to the internal standard, deuterated anthracene, and is similar to the cause just discussed. The deuterated anthracene, used for quantitation of the surrogate standards, has a relatively high volatility. Therefore, it is possible that some deuterated anthracene evaporated into the gaseous headspace in the 7 mL vial. Thus when the concentration of deuterated anthracene was assumed for calculations, the concentration was wrong. The actual concentration would be less than the assumed amount because some deuterated anthracene evaporated out of the solvent. This would cause recoveries of the surrogate standard to be more than anticipated, that is, more than 100%.

Recoveries for surrogate standard (excluding naphthalene) never fell below 50%, therefore, all the samples analyzed had acceptable recoveries. None of the data from the samples was discarded due to insufficient sample recovery.

4.6.4. Sample Contamination

Sample contamination testing involves testing several different types of blanks, as described in Section 3.5.4. The blanks which were tested included glassware blanks, method blanks, standard blanks, and solvent blanks.

4.6.4.1. Glassware and Glassware-Standard Blanks

For a glassware blank run, the entire method used to test a sample for aqueous phase concentration was carried out, however no sample matrix, or contaminated soil, is added. This means that any detectable PAH compounds which are found come from either PAHs in the solvent or PAHs on the glassware. The possibility of solvent contamination is very low (see section 4.6.4.4), therefore, the main source of PAH contamination is from the glassware itself.

Three glassware blanks were conducted. The information from glassware blanks does not give an indication of how much PAHs exist on the glassware, but it indicates whether or not PAHs are present as residue on the glassware. For the three samples run, there were certain PAHs present in all cases. Deuterated chrysene was present in one sample, but the peak area found was only 0.6% of the size of the average peak detected for PAH aqueous phase quantitation. Therefore, it was felt this level of contamination was negligible.

A glassware-standard blank run involves running through the entire method used to test a sample for aqueous phase concentration, again adding no contaminated soil. However, the standards are added for this case to quantitate any PAH residue found on the glassware.

A total of sixteen glassware-standard blanks were run. Of these, four showed no PAH contamination from the glassware. Of the remaining 12, the peak size abundance data is listed in Table 4.17. From this data, it is clear that one sample (sample 3 in Set 1) was the worst case. The peak abundance for the glassware contamination was compared to that for an actual sample (with the contaminated soil added) to obtain an estimate of the fraction of PAHs due to the contaminated glassware. When data from Sample 3 is included in the average value for all the blank samples, the percentage of contamination is fairly high, reaching 6.5% for acenaphthalene and 7.6% chrysene. When the data for Sample 3 is not included in the averages, the percent contamination is less. No contamination for naphthalene exists, and only chrysene and benz(a)anthracene are above 5% contamination. This means that the level of contamination is generally acceptable (under 5%).

When the data from Sample 3 only is used as a worst-case scenario, the percent contamination in that sample is excessive and unacceptable. The average level for Sample 3 was 20% contamination. One possible explanation for the excessive contamination in this sample is that there were other users of the GC/MS system who used the GC intermittently with samples run for this thesis. Some of the compounds these users were quantitating were heavy hydrocarbons, which have a high affinity for residing in the GC column and require very high temperatures in order to be driven out of the GC column.

Table 4.17. Sample PAH Contamination on Glassware

	Trial # for Glassware with Standards Blank												Average peak area	AVERAGE % PAHs on glassware	Worst peak area	WORST % PAHs on glassware
Compound	1	2	3	4	5	1	3	4	5	6	8	9				
Naphthalene	0	0	2000	0	0	0	0	0	0	0	0	0	166.7	2.8%	2000	33.3%
Acenaphthalene	2500	1500	6000	1500	0	200	0	0	0	0	0	0	975.0	6.5%	2500	16.7%
Acenaphthene	5000	2500	12000	2500	1200	300	200	0	500	400	0	400	2083.3	0.8%	12000	4.8%
Phenanthrene	35000	15000	60000	12000	600	1000	700	500	1000	1000	400	900	10675.0	2.4%	60000	13.3%
Fluoranthene	25000	15000	30000	5000	600	200	200	600	400	500	400	400	6525.0	3.8%	30000	17.6%
Pyrene	15000	8000	20000	2000	600	100	100	600	400	500	400	400	4008.3	4.0%	20000	20.0%
Benz(a)anthracene	3000	2000	2500	1500	1500	200	200	500	200	200	200	200	1016.7	7.3%	3000	21.4%
Chrysene	3000	3000	3000	1500	1500	200	200	500	200	200	200	200	1141.7	7.6%	3000	20.0%
Benzo(a)pyrene	0	0	0	0	1300	0	0	100	0	0	0	0	116.7	3.9%	1300	43.3%

Excluding run 3:

Compound	Average peak area	AVERAGE % PAHs on glassware	Worst peak area	WORST % PAHs on glassware
Naphthalene	0	0.0%	2000	33.3%
Acenaphthalene	518.18	3.5%	2500	16.7%
Acenaphthene	1181.82	0.5%	12000	4.8%
Phenanthrene	6190.91	1.4%	60000	13.3%
Fluoranthene	4390.91	2.6%	30000	17.6%
Pyrene	2554.55	2.6%	20000	20.0%
Benz(a)anthracene	881.82	6.3%	3000	21.4%
Chrysene	972.73	6.5%	3000	20.0%
Benzo(a)pyrene	127.27	4.2%	1300	43.3%

Also, the injection septum of the GC became very dirty and contaminated after only one injection of the other samples due to their high affinity for the plastic injection septum and injection port liner. For five of the glassware-standard blanks, two injections were made. One was before cleaning the injection septum and baking the GC column, and one after. The samples injected after cleaning the septum and baking the column to drive out contamination in the column generally resulted in a much better sample run. For 3 of the 5 sample runs with two injections, the sample was found to contain no contamination after the second run, that is, after the GC was cleaned. These same samples appeared to contain much contamination when run through the GC before it was cleaned.

After this realization was made, every effort was made to ensure the GC was cleaned before the samples for these experiments were injected. This involved baking the column at 300°C for several hours, and changing the injection port liner and septum before a set of GC runs. This ensured a minimum of sample contamination.

As Sample 3 was only one case out of the sixteen, it was felt that the data would not be adjusted for sample contamination as the average contamination level, discarding Sample 3, was less than 5% which is acceptable.

4.6.4.2. Solvent Blanks

A solvent blank involves running the solvent through the GC/MS to determine if there exist any interfering compounds in the solvent. Every time a new batch of solvent is prepared, a solvent blank was run to ensure the solvent is contaminant free.

A total of 18 solvent blanks were run throughout the duration of the experiments. Of the 18 runs, only 3 found any PAH contamination. One of these sample was run just after another user had finished with the GC/MS system. The contamination could have been residue in the GC/MS system from that user.

The other two samples which had PAHs had only minute amounts. One had contamination for phenanthrene, and fluoranthene. However, the peaks for these compounds were approximately 0.07% and 0.3% of the average peak size detected for a real run for these compounds. The second sample with detectable contamination had a peak size of approximately 0.7% of the average peak size detected. Therefore, it is felt that the level of contamination found in the solvent was a negligible amount that does not affect the overall values obtained for the data.

4.6.4.3. Standard Blanks

A total of 15 standard blanks were run. This means the standard was placed in a GC vial, and brought up to volume in the vial with fresh dichloromethane solvent. This sample was then injected into the GC/MS to quantitate any contamination which may originate from the standard or solvent added. However, as Section 4.6.4.2. discusses, contamination in the solvent was negligible. Therefore, any contamination found in standard blanks originates mainly from the standard.

The data from the standard blanks is found in Table 4.18. Out of the 15 samples, 8 contained acenaphthene contamination, 10 contained phenanthrene contamination, 6 contained fluoranthene and/or pyrene contamination, all contained benz(a)anthracene and/or chrysene contamination, and 8 contained benzo(a)pyrene contamination.

The average amount of contamination found for acenaphthene, phenanthrene, and fluoranthene/pyrene was acceptable for averages calculated (below 0.5% for each), and even for the worst case sample, the average level of contamination was 1% or less. This represents a negligible level of sample contamination. No adjustment of the data was required to account for sample contamination from these PAHs.

For benz(a)anthracene and/or chrysene and the benzo(a)pyrene contamination, the levels were very high. The percentage level for averages was above 10% for both, and for the worst case sample, the percentage level was above 20%. This represents unacceptable sample contamination.

As the data screening process showed, the coefficients of variation for these compounds were too high for them to yield useful statistical data. Also, there is too much sample contamination for these compounds. These are two reasons why these compounds were not statistically analyzed.

Table 4.18. Percent PAH Contamination in Standard Blanks

	Blank Sample Number									Average peak area	Worst peak area	Average % PAHs in standard	Worst % PAHs in standard
PAH Compound	1	2	3	4	5	6	7	8					
Acenaphthene	2500	2500	1500	1000	500	2000	200	2500		29188.9	2500	11.7%	1.0%
Phenanthrene	200	200	200	400	600	600	600	500		50366.7	600	11.2%	0.1%
Fluoranthene	1000	600	200	200	200	200	0	0		19155.6	1000	11.3%	0.6%
Benz(a)anthracene	1500	800	600	600	400	400	2000	3000		2700.0	3500	18.0%	23.3%
Benzo(a)pyrene	2000	1500	1500	500	500	1400	1500	2000		3506.8	2000	116.9%	66.7%

	Blank Sample Number (continued)						
PAH Compound	9	10	11	12	13	14	15
Acenaphthene	0	0	0	0	0	0	0
Phenanthrene	500	500	0	0	0	0	0
Fluoranthene	0	0	0	0	0	0	0
Benz(a)anthracene	3000	2000	1000	1000	2500	3000	3500
Benzo(a)pyrene	0	0	0	0	0	0	0

4.6.5. Response Factors for the Mass Spectrometer

As discussed in Section 4.6.3. on sample recoveries, response factors were necessary for the mass spectrometer (MS) used for these experiments. The calculation of response factors for the sixteen PAHs was similar to the calculation of response factors for the deuterated anthracene internal standard as described in section 4.6.3. A given mass of surrogate deuterated PAH standards was placed in a GC vial, and a given mass of PAH standard mix (containing the sixteen priority PAHs) was added. The vial was then filled with pure solvent and run through GC/MS analysis. The peak areas of the surrogate standard were compared to those of the deuterated standard, and response factors were calculated relating the peak areas according to the ratio of masses used.

The table of calculated response factors (RF's) is Table. 4.19. Two sets of factors were calculated, each set containing different mass ratios of the 16 PAH mix to the surrogate standards. The calculated RF's vary widely, as indicated by the large standard deviations for anthracene, benz(a)anthracene, chrysene, indeno(1,2,3-c,d)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene. The RF values calculated were compared to the RF values previously calculated by Zemanek (1994). Most of the compounds which were accepted for statistical analysis had RF's that corresponded closely to those previously determined.

The RF's shown in Table 4.19. were calculated after several experimental runs had already been quantitated using the previously determined RF's. Therefore, all the PAH quantitation calculations were carried out using the previously determined RF's. This is acceptable, as the objective of the experiments was to measure relative changes in aqueous phase PAH concentrations. If the RF's are held constant throughout the experiments, any relative change should not be affected.

The information from the calculation of the new RF's provides some additional information. The mass spectrometer response was not linear. The chromatographic peaks obtained to determine the RF's were not high quality. Lastly, the GC was not running at optimal conditions for optimal peak integration, because some chromatographic peaks were very close to each other and laying over top each other.

Table 4.19. Response Factor Data

	Group 1				Group 2								
PAHs: Standard ratio->	1:2	3:4	1:4	1:1	5:2	5:1	15:2	1:2		Standard	M.Z.	M.Z. value minus	% Error Average from
Compound	Set 1	Set 2	Set 3	Set 4	Set 1	Set 2	Set 3	Set 4	Average	deviation	value	Average	M.Z. value
Naphthalene	0.899	0.881	0.791	0.830	0.678	0.690	0.698	0.813	0.785	0.09	**0.948**	0.16	-20.7%
Acenaphthalene	0.644	0.621	0.564	0.605	0.548	0.507	0.489	0.850	0.603	0.11	**0.561**	-0.04	7.0%
Acenaphthene	0.873	0.865	0.712	0.752	0.713	1.053	0.750	0.843	0.820	0.11	**0.919**	0.10	-12.1%
Fluorene	0.797	0.772	0.704	0.718	0.648	0.609	0.597	1.001	0.731	0.13	**0.870**	0.14	-19.1%
Phenanthrene	0.874	0.820	0.895	0.968	0.610	0.611	0.622	0.738	0.767	0.14	**1.046**	0.28	-36.3%
Anthracene	1.545	1.411	1.371	1.355	1.067	0.832	0.866	3.562	1.501	0.87	**0.939**	-0.56	37.4%
Fluoranthene	0.463	0.493	0.583	0.584	0.309	0.337	0.374	0.234	0.422	0.13	**0.992**	0.57	-135.0%
Pyrene	0.702	0.724	0.727	0.748	0.586	0.628	0.653	0.626	0.674	0.06	**0.515**	-0.16	23.6%
Benz(a)anthracene	2.003	1.670	1.558	1.709	3.709	2.041	1.693	2.580	2.120	0.72	**1.154**	-0.97	45.6%
Chrysene	1.691	1.387	1.986	2.237	3.359	1.500	1.422	2.121	1.963	0.65	**0.791**	-1.17	59.7%
Benzo(b)pyrene	1.092	0.999	1.070	0.970	0.587	0.509	0.496	0.527	0.781	0.27	**0.748**	-0.03	4.2%
Benzo(k)pyrene	0.604	0.605	0.604	0.559	0.293	0.303	0.318	0.340	0.453	0.15	**0.748**	0.29	-65.0%
Benzo(a)pyrene	1.481	1.295	1.241	1.156	0.870	0.681	0.639	1.721	1.135	0.38	**0.934**	-0.20	17.7%
Indeno(1,2,3-c,d)pyrene	3.263	2.533	3.546	2.942	1.759	1.187	1.040	3.851	2.515	1.08	**0.914**	-1.60	63.7%
Dibenz(a,h)anthracene	4.968	3.771	4.260	3.078	2.661	1.538	1.326	8.790	3.799	2.38	**1.219**	-2.58	67.9%
Benzo(g,h,i)perylene	2.452	2.224	2.335	1.772	1.198	0.926	0.820	2.074	1.725	0.66	**1.035**	-0.69	40.0%

Note: the M.Z. value is the response factor value previously calculated by Zemanek (1994).

5.0. DISCUSSION

5.1. Results of Hypothesis Testing

As stated in Section 2.5, the hypotheses which this thesis set out to test are:

(1) the freezing and thawing of a creosote contaminated soil increases the availability of the creosote to the aqueous phase;

(2) freezing may induce significant movement of PAHs through the soil column tested;

(3) freezing with a high soil moisture content will have a significantly greater effect than freezing with a low moisture content in terms of causing increased PAH availability following freezing;

and

(4) a fast freezing rate will be significantly more effective than a slow freezing rate in terms of causing increased availability of PAHs following freezing.

The factorial analysis examined the factors of freezing rate, moisture content, and location of contamination, and thus tested the second, third, and fourth hypotheses. A one-way ANOVA tested the first hypothesis.

The factorial analysis was conducted before the one-way ANOVA to test for freezing. In the factorial analysis, certain factors were found to be insignificant. Therefore, when the ANOVA calculations were done, the values of PAH aqueous phase concentrations were averaged for conditions which were found to be insignificant by the factorial analysis.

The full results of the factorial calculations are found in Appendix B-1 for clay, and Appendix B-2 for sand. Summary tables of the results are shown in Table 5.1. for sand, and in Table 5.2. for clay.

The full results of the one-way ANOVA for the effect of freezing are found in Appendix C-1 for clay and Appendix C-2 for sand. Summary tables of the results of the ANOVA are Table 5.3. for sand and Table 5.4. for clay.

Table 5.1. Significance Level from Factorial Calculations using F Test (ANOVA) For Sand Soil

	Source of variation		
PAH Compound	Moisture	Location	Freezing rate
Total PAH's	no	no	no
Naphthalene	yes-1%	no	no
Acenapthene	no	no	no
Fluorene	no	no	no
Phenanthrene	no	no	yes-5%
Fluoranthene	yes-5%	no	no
Pyrene	no	no	no
Benzo(b+k)pyrene	no	no	no

Table 5.2. Significance Level from Factorial Calculations using F Test (ANOVA) For Clay Soil

	Source of variation			
PAH Compound	Moisture	Location	Moisture & location	Freezing rate
Total PAH's	yes-1%	no	no	no
Acenaphthene	yes-1%	no	no	no
Fluorene	yes-1%	no	yes-5%	no
Phenanthrene	no	no	no	no
Fluoranthene	no	no	no	no
Pyrene	yes-1%	no	no	no

Note: % value denotes the significance level for the source of variation

Table 5.3. Significane Level for Freezing Using ANOVA for Sand Soil

PAH Compound	**Experimental Conditions**		
	Low moisture	High Moisture	Both moistures
Total PAHs			no
Naphthalene	no	no	
Acenapthene			no
Fluorene			no
Fluoranthene	no	no	
Pyrene			no
Benzo(b+k)pyrene			no
	Slow Freezing	Fast Freezing	
Phenanthrene	no	no	

Table 5.4. Significance Level of Freezing Using ANOVA for Clay Soil

PAH Compound	**Experimental Conditions**		
	Low Moisture	High Moisture	Both moistures
Total PAHs	no	yes-10%	
Acenaphthene	no	yes-5%	
Fluorene	no	yes-5%	
Phenanthrene	no	no	
Fluoranthene			no
Pyrene	no	yes-10%	

Note: % value denotes significance level for the source of variation

5.1.1. Discussion of the Results of Factorial Analysis

5.1.1.1. Sand Soil

The results of the factorial calculations for the highly contaminated sand soil indicate general disagreement with hypothesis 2, 3, and 4.

Location of contamination following freezing was not significant for any PAH compound analyzed for both the low level of contaminated soil (the clay) and the higher level of contaminated soil (the sand), indicating disagreement with hypothesis 2. However, it is important to note that the method of detection for mobilization was limited in that it only involved measurement of the aqueous phase PAH concentrations. A more appropriate hypothesis, given the method of testing, is that the location of soil sampling following freezing, given sampling at the top and bottom of the compacted soil, may show an effect on the aqueous phase PAH concentrations. This hypothesis was found to be untrue.

One reason to explain why the hypothesis is untrue is that true unidirectional freezing was not achieved. In order to freeze the entire sample, a -2°C temperature plate was placed on top of the compacted soil sample. This plate caused freezing rates at the top and bottom of the soil to be relatively close to one another, as shown in Figure 3.4. where the freezing rate at the top of the soil is virtually the same as at the bottom. The slowest freezing rate occurred in the middle of the sample. As a result, possibly the middle of the sample should have been tested for aqueous phase PAH concentrations, and compared to the bottom of the soil sample aqueous phase PAH concentrations. If exclusion was occurring, it may have pushed solutes to the middle of the sample where the freezing rate was the slowest.

Another possible explanation for the experimental results not confirming the hypothesis is that for the conditions evaluated in these experiments, freezing simply does not induce significant mobilization of PAHs through the soil. The main mechanism expected for hydrocarbon mobilization is volatilization or exclusion induced by unidirectional freezing. For creosote, exclusion was expected to be the main mechanism since volatilization is not a dominant process. Exclusion occurs when water freezes and pushes out or excludes solutes ahead of the forming ice. However, because such a limited amount of PAHs are found in the aqueous phase, such as 1% or less on average (Zemanek, 1994), it is likely that exclusion and diffusion of the PAHs through the soil is not a dominant physical process and occurs on a very small, undetectable scale. Therefore, no detectable difference in PAH aqueous phase concentrations are found between the top and bottom of the soil samples.

For hypothesis 3, freezing with a high moisture content was found to be significant for naphthalene at the 1% significance level, significant for fluoranthene to the 5% level, and insignificant for the other PAHs analyzed. It is important to note that for sandy (coarse-grained) soils, significant structural reorganization of the soil grains caused by freezing is not expected to occur (Sego, 1995). However, small changes may occur.

Naphthalene has the highest solubility of the PAHs studied, and therefore, it follows that freezing coupled with a high moisture content does permit more naphthalene to dissolve into the aqueous phase. The high moisture content coupled with freezing is likely causing some soil structural shifting, thus permitting more naphthalene to become available to the aqueous phase. Because the solubility is relatively high compared to the other PAHs, the change in naphthalene aqueous phase concentration is detectable. The magnitude of aqueous concentrations for fluoranthene were fairly high as compared to the aqueous concentrations for the other PAHs tested. This is likely the reason why a small change in aqueous availability caused by freezing with a high soil moisture content was detectable for fluoranthene, although the level of significance is less than that for naphthalene.

For the other compounds which do not show freezing with a high moisture content to be a significant variable, their factorial results disagree with hypothesis 3. The most likely reason is that not enough structural changes are occurring to permit more availability of the PAHs to the aqueous phase. Also, other mechanisms may be acting which reduce the amount of PAHs that dissolve in the aqueous phase. As discussed later in Section 5.3., the PAHs are not dissolving up to their solubility limits.

For hypothesis 4 regarding the significance of freezing rate, only one compound, phenanthrene, showed freezing rate to be significant. The data in the TOTALS column for the factorial analysis for phenanthrene (found in Appendix B-2) indicates that the fast freezing rate permits more phenanthrene to be found in the aqueous phase. However, the correctness of this result is questionable. If freezing rate is truly a significant effect for phenanthrene, why is it not significant for other compounds?

The coefficient of variation associated with phenanthrene is approximately 18%. By looking at the factorial data for phenanthrene, some values appear to be extreme. The average value for the entire set of data is 14.26. When several extreme values are present, Chauvignot's criteria may permit these extreme values to lie within the acceptance range. However, the value of 9.02 varies 37% from the mean value, the value 18.86 varies by 32%, and the value 19.12 varies by 34% from the mean value. All other values are within 25% of the mean. The extreme values may be caused by variation in the soil samples or laboratory error. However, if these values are changed, the factorial results change significantly. If 9.02 is replaced by the average of the other two values for that row of data, and 18.86 and 19.02 are replaced by the remaining value for that row, the new results show that no factors are significant (the new calculations are found in Appendix B-2 following the factorial calculations for phenanthrene) The newly calculated results agree with the other PAH results in that freezing rate is not not a significant variable for the highly contaminated sandy soil.

Another possibility for the relative insignificance of freezing rate is that the freezing rates did not vary enough from sample to sample for a true difference to be seen. All the freezing rates were relatively close to one another, and it was difficult to control the freezing rates actually achieved. This is discussed in detail in Section 5.1.1.2.

5.1.1.2. Clay Soil

The factorial results for the clay soil indicate general agreement with hypothesis 3 and disagreement with hypothesis 2 and 4.

Location of sampling for aqueous phase PAH concentrations was expected to be significant, however, the results indicate disagreement with this hypothesis. Reasons for this are the same as for the highly contaminated sandy soil. That is, the main mechanism for mobilization is exclusion from the aqueous phase as soil water freezes. However, as such small PAH concentrations are found in the aqueous phase, detectable differences in aqueous phase concentration due to exlusion are not observed. Also, the location of sampling should have been a comparison between the locations with the fastest and slowest freezing rates.

Moisture content is a significant variable for five of the six PAH compounds analyzed, fluoranthene being the exception. Moisture content was significant at the 1% level for the sum total PAHs, acenaphthene, fluorene, and pyrene, and at the 5% level for phenanthrene. These results, indicating the significance of moisture content, are expected since many other researchers found high moisture contents caused maximum structural reorganizations in clayey materials after freezing (see Section 2.3.1.). Also, similar to the reasoning for the sand soil, an excess of PAHs in the clay soil is assumed. Therefore, the PAHs should theoretically dissolve up to their aqueous solubility. When more water is present, more PAHs should dissolve into the water. The factorial results show agreement with this, except for fluoranthene.

For pyrene to exhibit significance of moisture content (at 1% significance level) and not fluoranthene is difficult to explain. The aqueous solubility for fluoranthene is approximately twice as high as pyrene. Therefore, if pyrene exhibits change in aqueous phase concentration when more water is present, fluoranthene should exhibit the same change. However, this is not the case and a possible explanation for this anomaly is difficult to postulate.

The coefficient of variation associated with fluoranthene, approximately 16% on average, is not excessive compared to the variation associated with the other compounds analyzed. However, there are some questionable data values which may be affecting the statistical results. For Run 1, the data for fluoranthene for the bottom of the cell contained a value which was 4.71 μg/g higher than the mean for that entire data set (for Run 1,9, and 17). The data for this particular set had a coefficient of variation of 22%, which is high. For Run 10 for the top of the soil sample, an outlier value was accepted. This value was 2.27 µg/g higher than the mean for that data set. For Run 10 for the bottom of the sample, an outlier was accepted which was 1.89 µg/g higher than the mean for that data set. In the data for Run 5 for the top of the sample, one value in the data set was present which was 3.70 µg/g lower than the mean value for that data set. Again for Run 5 for the bottom of the sample, the data contained a value which was 2.99 µg/g lower than the mean value for that data set. For Run 6, a value was found which was 2.29 µg/g lower than the mean value for that data set.

When all of these values are deleted and the calculations are re-done, the results indicate that moisture content is significant at the 10% level. If these data omissions are not made, the magnitude of the effects for moisture content, freezing rate, the interaction between moisture content and location, and the interaction between freezing rate and moisture content, are all approximately the same magnitude (effects = 0.60-0.75). For tests where the interactions are significant, only those tests on the main effects indicating significance are meaningful. Insignificant main effects in the presence of significant interaction may be a result of masking. Masking occurs when a significant interaction causes the true effects to be undetected in the statistical analysis (Walpole and Myers, 1989, and Box, Hunter, and Hunter, 1978). Because the freezing rate-moisture content and location-moisture content interaction effects are significant (they vary significantly from the magnitude of other effects which are close to zero), the true effect of moisture content may be masked. The data has enough variability that the true effects cannot be detected.

Freezing rate was not found to be significant for any of the PAHs analyzed. This is in disagreement with hypothesis 4. However, there is one logical reason why freezing rate was not significant and it is that the freezing rate was not sufficiently varied to have an effect. For several previous researchers studies, freezing rate was found to be a significant variable. However, these studies indicate that the magnitude of freezing rates used were 1.5°C per hour (Chamberlain and Gow, 1979); 0.073°C per hour (Chamberlain, 1990); 0.03°C per hour (Konrad, 1989); and 0.02°C per hour (Ayorinde, *et al.*, 1989).

The average freezing rates used in these experiments for the clay sample varied considerably from those of previous researchers. As Table 4.3. showed, the slow freezing rates for the clay varied from 19.8°C per hour to 15°C per hour. For the fast freezing rate, the rate varied from 15.6°C per hour to 9.24°C per hour. The rates actually used vary from 6 to 1000 times difference from those other researchers used, by the most extreme comparisons.

Also, for the bottom of the sample, the average fast freezing rate was slower than the average slow freezing rate. This was true for the middle and top of the sample as well. However, this may be due to the rates for Run 2, 10, and 18 being incorrect. The temperature data for Run 2, 10, and 18 was recorded with an older computer system that only recorded the data every 2 hours as opposed to the computer system used for the other samples which recorded temperature information every five minutes. Therefore, the temperature data points for Runs 2,10, and 18 are not nearly as complete as the other data sets and are highly questionable. When the data for run 2, 10 and 18 is discarded, the average freezing rates increase substantially. The fast rates become larger than the slow freezing rates, which is the desired outcome. However, the fast and slow rates still do not vary significantly, varying only by a maximum of approximately 25%. With such a low variation between the fast and slow freezing rates, it is not surprising that freezing rate is not a significant variable. If the rates varied significantly, perhaps by 10 or 100 times, a difference may be detectable.

The rates used were limited by the equipment used for freezing. The baths could be set to any temperature, however, the temperature remained fixed. The temperature could not be decreased as a function of time automatically. The operator would have to manually reduce the temperature periodically to achieve slower freezing rates.

The freezing equipment was highly susceptible to environmental conditions as well. For example, the baths would get colder when the light in the temperature controlled (4°C) room was turned off. Opening and closing the door of the temperature controlled room would affect the bath temperatures slightly. Even though the temperature bath was set to a single temperature, the temperatures still displayed some variability.

There was a significant interaction effect between moisture and location for fluorene which theoretically means that for different locations in soil, the magnitude of the effect of moisture is different. As this interaction effect was not significant for any other PAH data set, it is unlikely a true significant interaction. It may be the result of variability in the data sets.

5.1.2. Discussion of the Results of ANOVA Analysis

5.1.2.1. Sand Soil

The results of the ANOVA analysis for freezing for the sandy soil are located in Table 5.3. As discussed earlier in Section 5.1., some factors were found to be insignificant for the factorial analysis. The values for these insignificant factors were grouped together and averaged. For example, location was insignificant by the factorial analysis, therefore, the top and bottom PAH concentrations for corresponding experimental conditions were averaged. Also, freezing rate was insignificant so the PAH concentrations for the fast and slow rates were averaged. These average values were then subsequently used in the ANOVA calculations for the significance of freezing. Separate ANOVAs were performed for variables which were found to be significant. For example, moisture content was significant for naphthalene. Therefore, one ANOVA was performed for the low level of moisture content and one for the high level.

By examining the results for the highly contaminated sandy soil, freezing was not found to be a significant variable for any of the PAHs analyzed. This disagrees with hypothesis 1 as it is stated. However, as discussed earlier, significant structural reorganization caused by freezing in sandy soils is not expected to occur (Sego, 1995). When the highly contaminated soil was first obtained, it was anticipated that it would contain significant quantities of clay sized particles. However, the grain size analysis showed it to contain a high portion of sand-sized particles. A suitable clay material with a high level of contamination could not be found with reasonable access.

As it was not anticipated that a sandy material would be tested, Hypothesis 1 should be revised for this soil material. Because freezing is not expected to have an effect on soil structural reorganization in a sand, the hypothesis should be that freezing will have no effect on aqueous availability of PAHs in a sandy soil. The experimental results agree with this revised hypothesis.

5.1.2.2. Clay Soil

The results of the ANOVA for clay soil are found in Table 5.4. Because moisture content was significant for five of the compounds analyzed, the ANOVAs were separated according to moisture content. The analyses performed for low moisture content consistently show no change in relative PAH aqueous concentrations following freezing, but the analyses for the high moisture contents do show a change for four out of five cases. However, the significance level is only 10% for the total PAHs and for pyrene, and 5% for acenaphthene and fluorene. Freezing does not appear to be a highly significant variable (1% significance would indicate a high level of significance).

As discussed in Section 2.2., PAHs in contaminated soil reside in several locations. The primary locations for creosote contamination are 70-95% in the oil phase (Zemanek, 1994), with this contamination being caught between soil particles and in dead-end pore spaces, in cracks and fissures in rocks, and also pooled on low-permeability lenses in the soil regime. No estimates could be found or are postulated for the percentage of creosote which is found between soil particles and in dead-end pores, which are the primary locations where soil freezing is hypothesized to have an effect.

One explanation for the relative insignificance of freezing is that a fairly low percentage of creosote is located in the soil where freezing can affect it. Freezing possibly does not open enough dead end pores or restructure the soil grains sufficiently to cause a measureable redistribution of PAH contamination. Any changes are non-detectable.

Another consideration for the lack of effect from freezing relates back to research by Chamberlain and Gow (1979). They found that freezing in silty clay reduced the volume of particles in pore spaces, and that the particles pulled more tightly together than previously (See Figure 2.4.). This may actually cause contaminant to become further trapped in the particles rather than released. It is possible that this is a dominant mechanism in some cases, thus canceling out any increased aqueous availability from freezing. Stepkowska and Skarzynska also found that freezing cycles in clays caused an increase in aggregate size, which means the soil particles pull tighter and closer together upon freezing (1989), possibly further trapping contamination.

Another potential reason for the insignificance of freezing is that the freezing temperatures were not low enough, and freezing of the complete sample did not occur. This was particularly true for the slow freezing rate, where some of the temperatures in the soil were in the range of -1.5°C and even slightly higher. Given that creosote contamination exists in the soil, it is possible that the freezing point of the soil water is depressed and temperatures well below 0°C are required to ensure complete freezing of the soil water. This means that the soil water in some of the samples for the slow freezing rate may not have been frozen, and ice crystallization never occurred in these samples. Ice crystallization is the mechanism which is hypothesized to cause the structural changes in frozen soils. If ice crystallization did not occur, no soil structural changes due to freezing are possible.

One final reason as to why freezing is not a significant variable involves the treatment of the soil before and after freezing. In order to obtain maximum aqueous phase concentrations without exceeding solubility, completely saturated soil conditions were necessary. However, in the batch equilibrium bottles, the soil and water turned into a slurry and the aggregated soil particles broke down. This likely destroyed any soil structure which existed, regardless of whether the sample was previously frozen or not. Therefore, the same aqueous phase PAH concentrations would be found before and after freezing because any structural changes which assisted to release PAHs were cancelled out when the soil was equilibrated with an excess of water.

Also, compacting the soil samples which were frozen may have had an effect on the contamination in the sample. By its very nature, compaction increases the density of a soil by pressing soil particles tightly together by expelling air from void spaces (Liu and Evett, 1987). This may subsequently drive contamination further into dead end pore spaces and rock fissures, which would increase the difficulty of aqueous accessibility. However, as was stated above, the soil equilibration procedure may have destroyed any existing soil structure regardless of what the structure was. Therefore, compaction would have little end effect on the accessibility of the aqueous phase to PAHs.

There are several explanations as to why freezing did not have a highly significant effect on the PAH contamination in the clay soil under the conditions studied for this thesis. However, it is important to note that other conditions may yield differing results.

5.2. Mass Balance Calculations

A true mass balance will not be performed for this experiment. A true mass balance would include calculations to determine the percentage of PAHs in every possible phase, including the oil phase, sorbed PAHs, any gaseous phase PAHs (possibly naphthalene), as well as aqueous phase PAHs. For the mass balance reported here, only the aqueous phase and the oil phase (Soxhlet extracted) can be accounted for.

Table 5.5. and Table 5.6. show the calculated averages for concentration of PAHs in the aqueous phase, grouped according to moisture content levels.

5.2.1. Mass Balance for Sand

For the sandy soil, a total of nine Soxhlet extractions and subsequent clean-ups were done to determine oil phase concentrations of PAHs. The total results of the Soxhlets are found in Appendix E-1. The results are averaged and presented in summary in Table 5.5, grouped according to moisture content.

From Table 5.5., the total amount of oil phase PAHs that partitioned into the aqueous phase was an average value of 0.38% for a low moisture content, and 0.28% for the high moisture content. These represent small fractions of the total PAHs present. The aqueous phase obviously does not access much of the PAHs present in the soil. For each individual PAH, the percentage of that PAH which partitions into the aqueous phase agrees with aqueous phase solubility theory, in terms of decreasing aqueous solubilities.

Table 5.5. Aqueous Percent of Total Concentration for SAND

	Normal moisture content			High moisture content		
PAH Compound	Average aqueous phase concentration µg/g	Oil phase concentration µg/g	% PAHs in aqueous phase	Average aqueous phase concentration µg/g	Oil phase concentration µg/g	% PAHs in aqueous phase
Naphthalene	5.40	8.17	66.15%	1.78	14.81	12.03%
Acenaphthalene	0.23	24.24	0.93%	0.21	31.66	0.68%
Acenaphthene	7.89	1111.04	0.71%	8.00	1229.66	0.65%
Fluorene	6.64	1017.00	0.65%	6.44	3182.23	0.20%
Phenanthrene	15.19	2800.35	0.54%	13.11	4038.71	0.32%
Anthracene	2.42	1079.00	0.22%	2.13	1513.72	0.14%
Fluoranthene	10.20	5284.05	0.19%	11.62	4043.22	0.29%
Pyrene	3.49	1529.61	0.23%	3.27	1523.66	0.21%
Benz(a)anthracnen	1.04	523.17	0.20%	0.75	473.38	0.16%
Chrysene	0.98	225.14	0.44%	0.62	273.81	0.23%
Benzo(b+k)pyrene	0.77	661.76	0.12%	0.75	664.78	0.11%
Benzo(a)pyrene	0.27	118.13	0.23%	0.17	126.57	0.14%
Indeno(1,2,3-c,d)pyrene	0.09	36.83	0.25%	0.05	31.74	0.16%
Dibenz(a,h)anthracene	0.03	14.83	0.20%	0.03	12.44	0.21%
Benzo(g,h,i)perylene	0.10	31.07	0.32%	0.06	34.76	0.16%
TOTALS	54.66	14464.39	0.38%	48.93	17195.14	0.28%

Table 5.6. Aqueous Percent of Total Concentration for Clay

PAH Compound	Normal moisture content			High moisture content		
	Average aqueous phase concentration μg/g	Oil phase concentration μg/g	% PAHs in aqueous phase	Average aqueous phase concentration μg/g	Oil phase concentration μg/g	% PAHs in aqueous phase
Naphthalene	0.42	5.42	7.75%	0.28	5.36	5.22%
Acenaphthalene	0.48	2.16	22.22%	0.67	2.27	29.52%
Acenaphthene	21.68	140.56	15.42%	23.32	138.46	16.84%
Fluorene	18.44	269.20	6.85%	19.91	206.32	9.65%
Phenanthrene	22.09	419.24	5.27%	25.56	384.97	6.64%
Anthracene	0.86	9.16	9.39%	0.18	23.37	0.77%
Fluoranthene	11.52	963.83	1.20%	10.55	739.95	1.43%
Pyrene	2.30	161.64	1.42%	2.79	171.66	1.63%
Benz(a)anthracene	0.09	0.00	0.00%	0.05	2.52	1.98%
Chrysene	0.28	36.04	0.78%	0.22	23.98	0.92%
Benzo(b)pyrene	0.31	53.77	0.58%	0.30	55.64	0.54%
Benzo(k)pyrene	0.34	57.41	0.59%	0.34	59.62	0.57%
Benzo(a)pyrene	0.04	4.71	0.85%	0.07	4.26	1.64%
Totals	78.85	2123.14	3.71%	84.24	1818.38	4.63%

The partitioning into the aqueous phase generally decreases as one looks down the list of PAHs (which are listed according to decreased solubility and increasing molecular mass). For the PAHs with higher molecular masses than anthracene, the concentration of the PAHs in the oil phase vary from one to the next, but the approximate percentage in the aqueous phase stays relatively constant (approximately 0.20%). A reason for this phenomena is not clear.

5.2.2. Mass Balance for Clay

For clay, quantitation of oil phase PAHs was performed for each run. This data is found in Appendix E-2. Average concentrations for aqueous phase and oil phase are reported in Table 5.6.

For the clay, the total proportion of oil phase PAHs that partitioned into the aqueous phase was 3.7% for a low moisture content and 4.6% for a high moisture content. However, the mass percentage of this soil which is PAH contamination is only approximately 1-1.5%. Therefore, 3.7% and 4.6% of that 1-1.5% are proportions of relatively low PAH contamination. The aqueous phase obviously did not access the bulk of PAH contamination in this soil.

5.3. Theoretical Aqueous Phase PAH Calculations

A logical study for this thesis research is to compare the PAH aqueous phase concentrations obtained experimentally to the PAH aqueous phase concentrations one could predict theoretically. Two methods of comparison are presented. The first is a comparison of the experimentally-obtained PAH aqueous phase concentrations to the aqueous solubilities for a single PAH compound in pure water. The second comparison is between the obtained PAH aqueous phase concentrations and PAH concentrations predicted by means of an equation based on Raoult's Law relating aqueous solubility and expected aqueous phase concentration. These two comparisons are presented in Sections 5.3.1. and 5.3.2.

5.3.1. Pure Water Solubility vs. Actual Aqueous Concentrations

Table 5.7. presents the comparison of pure water PAH solubilities versus the experimentally obtained aqueous concentrations. In Table 5.7., the single compound, pure-water aqueous solubilities as found in the literature (Zemanek, 1994; Aldrich Chemical Co., 1994; and Merck Index, 11th Edition, 1989) for each respective PAH are listed in the first column. In the next four columns, the g per litre (g of PAH per L of water) measured according to the procedure described in Section 3.4.1. is reported for each respective experimental soil moisture condition. This table permits a comparison which considers the actual experimentally obtained aqueous phase dissolution for each PAH from bulk oil-phase creosote to the solubility of each individual PAH in pure water as obtained in the literature.

For the sandy soil, Table 5.7. shows that the PAH concentrations are much lower than the solubility values for naphthalene to anthracene. This means these PAHs are not dissolving up to their individual solubility limits. For compounds heavier than anthracene, the trend is reversed as the obtained PAH concentrations appear to be greater than or approximately equal to their solubility limits.

Considering each PAH individually suggests that some phenomena is not permitting the PAHs lighter than fluoranthene to dissolve up to their aqueous solubility limits. Some possibilities include the water not being in adequate contact with the creosote. This could arise if large pools of oil phase were present because dissolution only occurs at the oil-water interface, which may be a limited interface. Also, adsorbed creosote may not permit full aqueous dissolution. Possibly large amounts of oil-phase creosote could be trapped in fractures and dead-end pores, reducing the amount of aqueous dissolution that occurs. Unfortunately, freezing the soil does not appear to assist in accessing this contamination in any significant amount detectable to the aqueous phase.

Also, the single compound aqueous solubilities listed in the first column in Table 5.7. (the literature values) are obtained experimentally by dissolving one single compound at a time in pure water under carefully controlled laboratory conditions. The aqueous dissolution studied for this thesis research was dissolution from a complex mixture of over

Table 5.7. Single PAH Compound Solubility in Pure Water vs. Actual Aqueous Phase PAH Concentrations for Sand and Clay

		SAND		CLAY	
		Low m.c.	High m.c.	Low m.c.	High m.c.
PAH Compound	Average Aqueous Solubility* mg/L	Aqueous conc. of PAH mg/L	Aqueous conc. of PAH mg/L	Aqueous conc. of PAH mg/L	Aqueous conc. of PAH mg/L
Naphthalene	32.5000	0.2702	0.0891	0.0042	0.0028
Acenaphthalene	3.9300	0.0113	0.0107	0.0048	0.0067
Acenaphthene	3.9300	0.3946	0.4000	0.2168	0.2332
Fluorene	1.9500	0.3319	0.3219	0.1844	0.1991
Phenanthrene	1.0530	0.7593	0.6555	0.2209	0.2556
Anthracene	1.0100	0.1208	0.1064	0.0086	0.0018
Fluoranthene	0.2625	0.5101	0.5808	0.1152	0.1055
Pyrene	0.1450	0.1747	0.1636	0.0230	0.0279
Benz(a)anthracene	0.0120	0.0519	0.0373	0.0009	0.0005
Chrysene	0.0040	0.0491	0.0308	0.0028	0.0022
Benzo(a)pyrene	0.0034	0.0046	0.0026	0.0004	0.0007
Totals	44.80	2.68	2.40	0.78	0.84

*from Zemanek (1994); Aldrich Chemical Company (1994); Merck Index (1989)

200 compounds including PAHs and other hydrocarbons which are present in creosote, from a natural soil setting.

For the clay soil, all of the PAHs studied exhibit lower dissolved concentrations than aqueous solubility data predicts. Possible explanations for this phenomena are similar to those given for the sandy soil, such as limited oil-water interfacial areas and the fact that the PAHs studied in the experiments are part of a complex mixture of compounds. Comparing the clay soil to the sand soil, the aqueous PAH levels were much lower for the clay in general. This is likely because there were much less PAHs available for aqueous dissolution in the clay than in the sand. The level of total petroleum hydrocarbon contamination (TPHC) in the clay was approximately 1-1.5% whereas the level of TPHC in the sand was one order of magnitude higher, 12-15% (as discussed in Section 3.1.).

The results listed in Table 5.7. provide a first approximation for the comparison between the expected aqueous concentrations and the determined aqueous concentrations. A more detailed calculation of theoretical concentrations is found in the following section.

5.3.2. Raoult's Law vs. Actual Aqueous Phase Concentrations

A more rigorous method of calculating theoretical aqueous phase concentrations is through the use of a derivation of Raoult's Law for partitioning between an aqueous phase and an organic liquid (Lee *et.al.*, 1992b) , which is:

$$C_w = X_o \times S_l$$

where: C_w = concentration of the chemical in aqueous phase in equilibrium with the organic phase (moles per litre)

X_o = mole fraction of the chemical in the mixture

S_l = aqueous solubility of the pure liquid chemical (moles per litre)

The aqueous solubility of a pure liquid chemical is readily available from literature as shown in the first column of Table 5.7. The mole fraction of the chemical in the mixture may be derived using a formula relating the mass fraction of each PAH in the creosote, the molecular mass of each PAH, and the average molecular mass of creosote. The equation follows:

$$C_w = \frac{MW_c \times M_{fc}}{MW_{PAH}} \times S_{lc}$$

where: C_w = concentration of the chemical in aqueous phase in equilibrium with the organic phase (moles per litre)

M_{fc}= mass fraction of each PAH of the creosote (g of creosote per g of soil)

MW_c= average molecular mass of creosote (g per mole of creosote)

MW_{PAH}= molecular mass of PAH compound (g per mole of PAH)

S_{lc}= supercooled liquid solubility for each PAH (moles per litre)

By multiplying the C_w value by the molecular mass of the PAH compound of interest (expressed as g per mole), the final concentration value obtained is expressed as g per L. Multiplying this value by 1000 produces units of mg/L, which are directly comparable to the values from Table 5.7. The final results of the calculation are shown in Table 5.8., along with the values of the experimentally obtained PAH aqueous phase concentrations for comparison purposes.

The mass fraction of each PAH in the creosote is the Soxhlet extractable PAH concentrations, expressed in g/g. The average molecular mass of creosote used is 420 g per mole. This value was estimated from the simulated distillation analysis of creosote taken from the site. The median atmospheric equivalent boiling point for the main fractions of creosote were related to the equivalent alkane (C_{30}) to estimate an equivalent molecular mass of approximately 420 (Pollard *et.al.*, 1993; and Pollard *et.al.*, 1994). The supercooled liquid solubility in moles per litre for each PAH is calculated by taking the antilog of values found in the last column of Table I in Lee *et.al.* (1992b).

By making a direct comparison between the actual concentration values obtained experimentally, it is obvious that only the aqueous phase concentration for naphthalene for clay compares reasonably well to Raoult's approximation. For all the other values, the experimental aqueous phase concentration values are all significantly higher than Raoult's

Table 5.8. Raoult's Law Theoretical Aqueous Phase Partitioning Calculations

PAH Compound Name (molecular mass in brackets)	Supercooled Liquid Solubility moles/L	SAND		CLAY		SAND		CLAY	
		Low m.c. **Raoult's** Aqueous Phase Conc. mg/L	High m.c. **Raoult's** Aqueous Phase Conc. mg/L	Low m.c. **Raoult's** Aqueous Phase Conc. mg/L	High m.c. **Raoult's** Aqueous Phase Conc. mg/L	Low m.c. **Actual** Aqueous Phase Conc. mg/L	High m.c. **Actual** Aqueous Phase Conc. mg/L	Low m.c. **Actual** Aqueous Phase Conc. mg/L	High m.c. **Actual** Aqueous Phase Conc. mg/L
Naphthalene (128)	0.000891	0.0031	0.0055	0.0020	0.0020	0.2702	0.0891	0.0042	0.0028
Acenaphthalene (152)	0.000095	0.0010	0.0013	0.0001	0.0001	0.0113	0.0107	0.0048	0.0067
Acenaphthene (154)	0.000105	0.0489	0.0541	0.0062	0.0061	0.3946	0.4	0.2168	0.2332
Fluorene (166)	0.000093	0.0399	0.1247	0.0106	0.0081	0.3319	0.3219	0.1844	0.1991
Phenanthrene (178)	0.000032	0.0372	0.0536	0.0056	0.0051	0.7593	0.6555	0.2209	0.2556
Anthracene (178)	0.000032	0.0147	0.0206	0.0001	0.0003	0.1208	0.1064	0.0086	0.0018
Fluoranthene (202)	0.000006	0.0143	0.0110	0.0026	0.0020	0.5101	0.5808	0.1152	0.1055
Pyrene (202)	0.000014	0.0091	0.0090	0.0010	0.0010	0.1747	0.1636	0.0230	0.0279
Benz(a)anthracene (228)	0.000001	0.0001	0.0001	0.0000	0.0000	0.0519	0.0373	0.0009	0.0005
Chrysene (228)	0.000005	0.0005	0.0006	0.0001	0.0001	0.0491	0.0308	0.0028	0.0022
Benzo(a)pyrene (252)	0.000001	0.0000	0.0000	0.0000	0.0000	0.0046	0.0026	0.0004	0.0007

Note: m.c.= moisture content

Molecular mass of creosote used = 420 g/mole

Conc.= concentration

law predicts. Most values are higher by an order of magnitude or more. Raoult's predicted values are also much lower than the average aqueous solubility values.

Possible reasons for these discrepancies are that values used in the adapted Raoult's equation may be incorrect. The average molecular mass for creosote is an approximation. The mass fraction values of the PAHs are limited by the efficiency of the Soxhlet extraction procedure, and measure only the oil-phase PAH concentrations. Also, when measuring aqueous dissolution from an actual field-collected soil sample, there are many external uncontrollable factors which may limit dissolution, such as partitioning to other more favorable phases such as the oil- and soil-phases, rather than the aqueous phase. Also, there is poor accessibility of the water phase to the contaminant due to pools of contamination and trapped contamination. It is expected that the experimentally obtained PAH aqueous concentrations would not match exactly theoretically derived concentrations.

6.0. CONCLUSIONS

Conclusions 1 to 4 address the results of the hypothesis testing. It is important to note that these conclusions are only valid for the conditions used for the experiments in this thesis.

1. Freezing and thawing of the sandy highly creosote-contaminated soil did not increase the aqueous phase concentrations of the 16 Priority PAHs. This is likely because freezing does not cause many soil structural changes in a coarse-grained soil.

The freezing and thawing of the clayey low-level creosote contaminated soil did increase the aqueous phase availability of four PAH compounds when coupled with a high moisture content, however, the increase in aqueous phase concentrations were not highly statistically significant (5-10% level of significance). Two of the six PAH compounds analyzed did not show significant increased PAH aqueous concentrations following freezing.

One possible explanation for the relatively low significance of freezing is that previous researchers had found that freezing may actually increase soil aggregation, and therefore further trap contamination rather than enhance a release. Also, the soil water may have had a depressed freezing point and therefore ice crystallization did not occur in every sample. A final reason involves the experimental pretreatments of the soil. This included compacting the soil, which compressed soil grains closer and may have potentially further trapped PAH contamination. Also, the batch equilibrium procedure which was required to maximize PAH aqueous phase concentrations may have destroyed any previously existing soil structure, therefore causing aqueous phase PAH concentrations before and after freezing to be very similar.

The significance of the final result, that freezing does not appear to make a difference to aqueous PAH availability, could also be interpreted as a positive finding because it implies that PAHs located in creosote contaminated sites will not move away from the site as a result of freezing and thawing. PAHs located at the site are highly likely to remain at the site for a lengthy period of time, due to their low aqueous solubilities and poor aqueous accessibilities.

2. Freezing the creosote highly contaminated sand and the creosote low-level contaminated clay did not induce mobilization of the PAHs in the direction of the advancing frost front.

Potential reasons for this include true unidirectional freezing was not actually achieved. Some solutes may have moved to the middle of the sample, and no sampling was done at this location. Also, there may not have been enough PAHs in the aqueous phase to be excluded as a result of freezing.

3. A high soil moisture content (in the order of field capacity) coupled with freezing had a significant effect on increasing aqueous phase PAH concentrations for the clay soil analyzed following freezing, which was expected. Moisture content was not a significant variable for the sand soil tested.

4. Freezing rate was not found to be a significant factor for any of the PAH concentrations studied. However, no real conclusions regarding freezing rate should be drawn. There was great difficulty in achieving consistent freezing rates, and the different freezing rates used varied by only approximately 25%. Some of the rates for fast freezing were actually slower than those for the slow freezing. Therefore, the freezing rate data obtained in this research is not reliable to draw conclusions regarding the effect of varying freezing rate on the soil.

5. There are many sources of errors for the measurements included in this thesis. Care was taken to ensure errors were minimized, however, it is impossible to completely eliminate error.

The error due to PAH residues on glassware used was approximately 5%, and varied from sample to sample. Care was required to clean the GC/MS for use before runs for these experiments to minimize artifacts arising from contamination arising from other users of the equipment.

Precision errors varied widely, from 5% up to 129%. These errors in replication could be due to the non-homogeneous nature of the soil, or other errors previously listed. Those PAH compounds which exhibited large coefficient of variation for their data sets (an average over 30%) were not statistically analyzed and no conclusions about the experimental outcomes were made for these PAHs. However, it should be noted that the aqueous phase PAH concentration data obtained for this research is indicative of concentration values obtained on "real" soil samples. "Real" refers to soil samples that have been taken from an actual contamination site, have been weathered, and have not been spiked or altered in any way from the field conditions.

Sources of error for aqueous phase PAH concentrations as a percentage of the total PAHs present includes uncertainty about the accuracy of response factors (RF) used for the calculation of aqueous phase and oil phase PAH concentrations. However, it is difficult to assess a magnitude for this source of error. By using the same RF's throughout the experiments and by making relative comparisons between PAH concentrations, the impact of the error due to RF's was minimized.

6. Water is confirmed as a very poor solvent for the sixteen priority PAHs. The fraction of PAHs which dissolved into the aqueous phase did not represent a significant fraction of the total PAHs present, representing approximately 0.30% for the sand and 4.0% for the clay. Even if freezing increased availability two fold or more, the aqueous phase is not effective for dissolving PAH compounds as a soluble limit is quickly reached. Dissolution and degradation of PAHs in the aqueous phase would be a very slow process if no other efforts are made to enhance the degradation process.

7. Aqueous dissolution of the PAHs up to their solubility limits is not occurring, according to approximate calculations based on solubility data. There are several factors which could be causing this, such as potentially low surface areas of oil globules exposed to water. Also, adsorption and trapped contamination may limit aqueous dissolution.

8. The results obtained for these samples under the conditions tested indicate that freezing and thawing soil would not be a useful pretreatment for creosote contaminated soil as a means of improving aqueous availability of PAHs. Because water is a very poor solvent for creosote PAHs (creosote is considered a "non-aqueous phase" material because of its extremely low solubility in water), the amount of PAHs that dissolve in water are very limited and do not represent a significant fraction of the oil phase PAH concentrations present.

9. Based on the observations for the conditions tested, freezing and thawing of soils will not be likely to improve the conditions for degradation of creosote compounds enough to warrant consideration of this natural process in risk assessments. The overall effect of freezing on improving creosote availability is not highly significant for clay after one freezing cycle, and the evidence for sand indicates no effect from one freezing cycle. Because the magnitude of structural changes caused by freezing are maximized in the first freezing cycle, freezing would not likely be a significant variable for the second or any future freezing cycles applied to the soil.

7.0. RECOMMENDATIONS

While the results for the conditions of this thesis showed no effects from freezing and thawing, other experimental conditions may yield different results. Therefore, the recommendations are broken down into two parts. The first part describes procedures which could have been done differently for this thesis research, and the second part describes recommendations for future further studies.

7.1. Recommended Alternate Procedures

One factor which may have biased the results was the type of soil used. Both the sand and clay used were surface soils, which means they were weathered soils which had likely undergone natural freeze thaw cycles in the winter. However, the results of the study may be different if a sub-surface soil was studied, that is, one which had never undergone a freeze-thaw cycle and was collected from below the active layer.

Another factor is the nature of the batch equilibrium process. In order to ensure PAH concentrations were below solubility limits, a large excess of water was equilibrated with the soils, causing the soil and water to turn into a slurry. The tumbling action likely broke apart any existing soil structure, thereby eliminating any effect from freezing on soil structure. However, the excess of water was required to ensure maximum solubilization of PAHs into the aqueous phase. A flow-through-soil column extraction may have yielded different results from the batch equilibrium extraction.

The frozen and unfrozen soil comparison was biased by the compaction of the frozen soil, while the unfrozen soil was not compacted. A more appropriate comparison would involve treating both soils identically, including compacting the unfrozen soil.

Compaction itself, however, may have pushed PAH contamination further into the soil structure voids, micropores, and fissures, because compaction by its very nature pushes soil particles closer together and compresses the soil by reducing the size of void spaces. Alternate methods to ensure uniform density which would not be as harsh on the soil structure as compaction should have been evaluated.

The high moisture content samples should have been subjected to standard procedures for moisture addition, such as permitting the moisture and soil to equilibrate for a 24 hour time period in a controlled environment. Also, moisture content itself should have been determined using the standard method because by the method used, moisture content is based on the varying quantity of moist weight of soil rather than the constant quantity of oven-dried soil (Liu and Evett, 1984). The standard method versus the method used would not cause great changes in moisture content, however, standard procedures should be followed.

7.2. Recommendations for Further Studies

As moisture content was found to be a significant variable for clay, a high moisture content when freezing soil should be evaluated. Previous research showed significant structural effects from freezing (as discussed in Section 2.3.2.) when the freezing rate was very slow, in the order of 0.5 cm of movement of the frost front per day. Therefore, further examination should be done to determine the effects of freezing soil when the moisture content is very high and the freezing rate is very slow. This may show increased availability of the sixteen priority PAHs following freezing. However, given the location and contamination in the soil and the low aqueous solubilities of the PAHs, it is likely that increased availability under different experimental conditions may still not be substantial.

Experimentation using a stronger solvent is another possibility for further testing. As water is such a weak solvent, particularly for heavy hydrocarbons such as the PAHs, a stronger solvent would not have the same limitations of water solubility. A surfactant, for example, may dissolve more of the compounds.

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Appendix A-1. Raw Data for Low-Level Contaminated Clay Soil

INTRODUCTORY COMMENTS FOR APPENDIX A-1 and APPENDIX A-2.

- The data contained in these appendices are the aqueous phase PAH concentrations for the 16 Priority PAHs.

- The data are grouped by experimental conditions. These are clearly labeled at the top of each page. For example, data for the LOW moisture content and SLOW freezing rate are grouped together. Data from one sampling location and for one set of experimental conditions appear all on the same page. Run numbers are for labeling purposes only, and were assigned arbitrarily.

- The location of where the sample was taken from is coded with letters which are clearly marked near the top of each page.
- Samples A, B, and C are always soil samples taken from the unfrozen soil.
- Sample D, E, and F are always samples from the top of the frozen soil.
- Sample G, H, and I are always samples from the bottom of the frozen soil.

- The statistical screening information is found near the right-hand side of each page. The standard deviation for the row of data and mean are located here, as well as Chauvignot's criteria. The LOW and HIGH values written under the heading "Chauvignot's range" represent the lowest possible acceptable value, and the highest possible acceptable value.

- For every data set, any values which are enclosed in a shaded box represent values which fall outside Chauvignot's range. For these values, a normal probability plot was drawn to check if the value fell on the normal curve. For the sake of brevity of this Appendix, the normal plots are not shown here. However, the results of the normal plots showed that for every outlying value, the normal curve drawn agreed reasonably well with the standard normal curve. Therefore, no data was discarded.

- Values enclosed in a box represent values which lie just outside Chauvignot's range, and are accepted values.

- "nd" denotes a non-detectable PAH concentration

- The average value of PAH concentration for a run is calculated for the three replicate analyses for that run. The average value is the value used for the factorial and ANOVA statistical analyses.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 1, 9, & 17: Moisture content is LOW and the Freezing Rate is SLOW
VALUES REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

PAH compound	Run 1A	Run 1B	Run 1C	Average	Run 9 A	Run 9 B	Run 9C	Average	Aqueous characterization averages	Standard Deviation	Mean	Chauvignot's Range Data points= 7 Low	Chauvignot's Range High
Naphthalene	0.40	0.28	0.33	0.34	0.51	0.46	0.28	0.42	0.37	0.09	0.37	0.22	0.53
Acenaphthalene	0.58	0.54	0.49	0.54	0.49	0.42	0.44	0.45	1.06	0.22	0.58	0.17	0.98
Acenaphthene	25.46	22.29	22.08	23.28	21.17	20.78	20.17	20.71	24.96	2.05	22.41	18.73	26.10
Fluorene	19.69	18.66	18.65	19.00	18.52	18.15	19.18	18.61	19.42	0.55	18.90	17.91	19.88
Phenanthrene	22.04	22.33	20.49	21.62	26.70	23.95	25.53	25.39	20.26	2.45	23.04	18.63	27.46
Anthracene	0.00	0.00	0.00	0.00	2.83	0.00	1.95	1.59	2.78	1.38	1.08	-1.40	3.56
Fluoranthene	13.40	12.82	13.43	13.21	11.11	9.01	9.80	9.97	7.29	2.39	10.98	6.68	15.27
Pyrene	2.53	2.38	1.98	2.30	2.62	1.95	2.09	2.22	3.03	0.39	2.37	1.66	3.08
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.20	0.06	0.10	0.12	0.48	0.18	0.12	-0.19	0.44
Chrysene	0.29	0.28	0.32	0.30	0.30	0.25	0.21	0.25	0.18	0.05	0.26	0.17	0.35
Benzo(b)fluoranthene	0.31	0.24	0.18	0.24	0.22	0.00	0.27	0.17	0.52	0.16	0.25	-0.03	0.53
Benzo(k)fluoranthene	0.31	0.25	0.19	0.25	0.23	0.32	0.27	0.27	0.53	0.11	0.30	0.10	0.50
Benzo(a)pyrene	nd	nd	nd	nd	0.03	0.03	0.04	0.03	0.26	0.12	0.09	-0.12	0.30
Indeno(1,2,3-c,d)pyrene	nd	nd	nd	nd	nd	nd	nd	nd	nd				
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd				
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	nd	nd	nd	nd				
Totals	85.01	80.07	78.13	81.07	84.91	75.38	80.32	80.20	81.15	3.46	80.71	74.48	86.94

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 1, 9, & 17: Moisture content is LOW and the Freezing Rate is SLOW
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

D,E,F SERIES: TOP OF CELL AFTER FREEZING

															Chauvignot's Range Data points=9	
PAH compound	Run 1D	Run 1E	Run 1F	Avg.	Run 9G	Run 9H	Run 9I	Avg.	Run 17D	Run 17E	Run17F	Avg.	Std.dev.	Mean	Low	High
Naphthalene	0.41	1.00	0.60	0.67	0.63	0.86	0.80	0.76	0.34	0.43	0.30	0.35	0.25	0.60	0.12	1.07
Acenaphthalene	0.64	0.61	0.67	0.64	0.48	0.48	0.44	0.47	0.48	0.48	0.57	0.51	0.08	0.54	0.38	0.70
Acenaphthene	25.01	24.78	24.60	24.79	20.57	21.77	20.40	20.91	20.54	20.24	23.10	21.29	2.05	22.33	18.42	26.25
Fluorene	18.16	18.11	19.67	18.65	18.20	18.14	17.11	17.82	17.48	16.38	19.14	17.67	0.99	18.04	16.15	19.94
Phenanthrene	18.91	19.39	19.94	19.41	23.19	24.25	23.22	23.56	21.86	21.98	21.54	21.79	1.85	21.59	18.06	25.12
Anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fluoranthene	12.38	13.60	12.54	12.84	10.74	9.58	10.17	10.16	10.12	10.37	9.48	9.99	1.47	11.00	8.19	13.80
Pyrene	2.33	2.50	2.40	2.41	2.38	2.07	2.20	2.22	2.29	2.26	2.06	2.20	0.15	2.28	1.99	2.56
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.08	0.04	0.05	0.05	0.02	0.03	0.15	0.06	0.05	0.04	-0.05	0.13
Chrysene	0.40	0.39	0.37	0.38	0.28	0.30	0.31	0.30	0.31	0.38	0.17	0.29	0.07	0.32	0.18	0.46
Benzo(b)fluoranthene	0.25	0.23	0.25	0.25	0.36	0.27	0.33	0.32	0.34	0.32	0.46	0.37	0.07	0.31	0.18	0.45
Benzo(k)fluoranthene	0.26	0.23	0.29	0.26	0.36	0.17	0.33	0.28	0.34	0.32	0.30	0.32	0.06	0.29	0.17	0.40
Benzo(a)pyrene	0.00	0.00	0.00		nd	0.04	0.02	0.02	nd	nd	0.11	0.04	0.04	0.03	-0.06	0.11
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	78.74	75.22	71.85	75.27	77.28	77.96	75.36	76.87	88.05	73.19	77.37	79.54	4.65	77.22	68.35	86.10

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 1, 9, & 17: Moisture content is LOW and the Freezing Rate is SLOW
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

G,H,I SERIES: BOTTOM OF CELL AFTER FREEZING

PAH compound	Run 1G	Run 1 H	Run 1 I	Avg.	Run 9G	Run 9H	Run 9I	Avg.	Run 17G	Run 17H	Run 17I	Avg.	Std.dev.	Mean	Chauvignot's Range Data points=9 Low	High
Naphthalene	0.63	1.45	1.16	1.08	1.54	2.09	1.13	1.59	1.21	0.66	0.63	0.83	0.49	1.17	0.23	2.10
Acenaphthalene	0.81	0.63	0.63	0.69	0.46	0.47	0.49	0.47	0.54	0.59	0.49	0.54	0.11	0.57	0.35	0.78
Acenaphthene	31.73	22.66	26.11	26.83	22.92	21.09	23.74	22.58	21.21	23.25	20.88	21.78	3.41	23.73	17.22	30.25
Fluorene	23.05	19.02	22.25	21.44	19.99	19.34	20.32	19.89	18.02	19.84	17.21	18.36	1.85	19.89	16.35	23.43
Phenanthrene	19.55	22.08	26.44	22.69	26.73	26.12	26.99	26.61	19.77	23.54	20.29	21.20	3.16	23.50	17.46	29.54
Anthracene	0.00	0.00	2.65	0.88	0.00	1.82	0.00	0.61	0.00	0.00	0.00	0.00	1.01	0.50	-1.43	2.42
Fluoranthene	14.08	16.11	10.54	13.57	11.86	11.16	11.85	11.62	7.99	10.53	8.53	9.01	2.53	11.40	6.57	16.23
Pyrene	2.40	2.99	2.53	2.64	2.49	2.54	2.51	2.51	1.98	2.54	2.15	2.22	0.28	2.46	1.92	3.00
Benz(a)anthracene	0.00	0.00	0.27	0.09	0.14	0.09	0.05	0.09	0.06	0.16	0.04	0.09	0.09	0.09	-0.07	0.25
Chrysene	0.43	0.47	0.20	0.36	0.27	0.25	0.29	0.27	0.20	0.23	0.18	0.20	0.10	0.28	0.08	0.47
Benzo(b)fluoranthene	0.31	0.34	0.22	0.29	0.41	0.23	0.31	0.32	0.32	0.43	0.30	0.35	0.07	0.32	0.19	0.45
Benzo(k)fluoranthene	0.30	0.35	0.22	0.29	0.41	0.25	0.34	0.33	0.32	0.43	0.30	0.35	0.07	0.32	0.20	0.45
Benzo(a)pyrene	0.00	0.00	0.10	0.03	0.06	0.10	0.03	0.06	0.04	0.09	0.02	0.05	0.04	0.05	-0.03	0.13
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd	nd	nd	nd	nd					
Totals	93.28	86.09	93.31	90.89	87.26	85.56	88.04	86.95	71.66	82.29	71.06	75.00	8.13	84.28	68.76	99.81

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 2, 10, & 18: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

												Chauvignot's Range Data points=7	
PAH compound	Run 2A	Run 2B	Run 2C	Average	Run 10A	Run 10B	Run 10C	Average	Aqueous characterization averages	Std. dev.	Mean	Low	High
Naphthalene	0.23	0.31	0.29	0.28	0.82	0.57	0.55	0.65	0.37	0.21	0.45	0.07	0.82
Acenaphthalene	0.54	0.45	0.46	0.48	0.37	0.47	0.57	0.47	1.06	0.23	0.56	0.14	0.98
Acenaphthene	22.18	20.29	22.94	21.80	21.84	18.92	22.02	20.93	24.96	1.92	21.88	18.43	25.33
Fluorene	17.43	16.56	17.08	17.02	18.84	19.06	19.47	19.12	19.42	1.21	18.26	16.09	20.44
Phenanthrene	19.92	17.88	18.77	18.86	18.41	23.83	25.27	22.50	20.26	2.84	20.62	15.51	25.73
Anthracene	0.00	0.00	0.00	0.00	1.97	1.84	1.70	1.84	2.78	1.16	1.18	-0.90	3.27
Fluoranthene	8.61	10.36	11.13	10.04	18.04	10.32	10.16	12.84	7.29	3.43	10.85	4.68	17.01
Pyrene	1.78	1.98	2.06	1.94	2.18	3.02	3.09	2.77	3.03	0.57	2.45	1.42	3.48
Benz(a)anthracene	0.05	0.00	0.00	0.02	0.00	0.46	0.24	0.23	0.48	0.22	0.18	-0.22	0.57
Chrysene	0.16	0.22	0.27	0.22	0.45	0.40	0.22	0.36	0.18	0.11	0.27	0.07	0.47
Benzo(b)fluoranthene	0.23	0.13	0.28	0.22	0.62	0.76	0.47	0.62	0.52	0.23	0.43	0.02	0.84
Benzo(k)fluoranthene	0.23	0.13	0.29	0.21	0.62	0.76	0.47	0.62	0.53	0.23	0.43	0.02	0.84
Benzo(a)pyrene	nd	0.03	0.01	0.02	0.09	0.19	0.09	0.12	0.26	0.10	0.11	-0.06	0.29
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	0.08	nd		nd				
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd				
Benzo(g,h,i)perylene	nd	nd	nd		nd	0.09	nd		nd				
Totals	71.37	68.34	73.58	71.10	84.25	80.77	84.33	83.12	81.15	6.49	77.68	66.00	89.37

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 2, 10, & 18: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

D,E,F SERIES: TOP OF CELL AFTER FREEZING

															Chauvignot's Range	
															Data points=9	
PAH compound	Run 2D	Run 2E	Run 2F	Avg.	Run 10D	Run 10E	Run 10F	Avg.	Run 18D	Run 18E	Run 18F	Avg.	Std. dev.	Mean	Low	High
Naphthalene	0.94	0.26	0.27	0.49	0.24	0.36	0.44	0.35	0.33	0.48	0.34	0.38	0.22	0.41	-0.01	0.82
Acenaphthalene	0.76	0.65	0.51	0.64	0.52	0.54	0.56	0.54	0.68	0.66	0.63	0.66	0.08	0.61	0.45	0.77
Acenaphthene	22.09	21.37	20.38	21.28	23.93	23.27	24.40	23.87	22.58	22.13	21.28	22.00	1.31	22.38	19.88	24.88
Fluorene	19.07	17.93	17.47	18.16	19.52	17.93	19.95	19.13	20.66	19.54	19.00	19.73	1.05	19.01	17.00	21.02
Phenanthrene	25.83	22.94	19.83	22.87	20.01	22.11	25.01	22.38	26.76	26.98	25.06	26.27	2.73	23.84	18.62	29.05
Anthracene	0.63	0.00	1.22	0.62	0.00	1.71	0.00	0.57	0.00	0.00	0.00	0.00	0.65	0.40	-0.85	1.64
Fluoranthene	9.66	8.86	8.81	9.11	11.81	8.52	9.71	10.01	9.84	9.56	9.10	9.50	0.97	9.54	7.69	11.39
Pyrene	2.92	2.51	2.12	2.52	2.48	2.48	2.83	2.60	2.88	2.59	2.46	2.64	0.25	2.59	2.10	3.07
Benz(a)anthracene	0.11	0.03	0.28	0.14	0.00	0.31	0.30	0.20	0.33	0.16	0.06	0.18	0.13	0.18	-0.08	0.43
Chrysene	0.24	0.22	0.16	0.21	0.56	0.31	0.31	0.39	0.29	0.31	0.31	0.30	0.11	0.30	0.09	0.51
Benzo(b)fluoranthene	0.19	0.28	0.35	0.27	0.37	0.52	0.22	0.37	1.20	0.29	0.24	0.58	0.31	0.41	-0.19	1.01
Benzo(k)fluoranthene	0.18	0.16	0.35	0.23	0.80	0.52	0.22	0.52	1.07	0.29	0.24	0.53	0.31	0.43	-0.17	1.03
Benzo(a)pyrene	nd	nd	0.09	0.09	0.27	0.16	0.14	0.19	0.00	0.00	0.00	0.00	0.10	0.09	-0.10	0.29
Indeno(1,2,3-c,d)pyrene	nd	nd	nd	nd	0.02	0.05	0.04	0.03	0.70	0.00	0.00	0.23	0.28	0.13	-0.40	0.67
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd				
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	0.04	0.05	0.05	0.72	nd	nd	0.72	0.39	0.27	-0.47	1.02
Totals	82.63	75.22	71.85	76.57	80.51	78.82	84.19	81.17	88.05	82.99	78.71	83.25	4.87	80.33	71.03	89.63

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 2, 10, & 18: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

G,H,I SERIES: BOTTOM OF CELL AFTER FREEZING

														Chauvignot's Range	
														Data points=9	
PAH compound	Run 2G	Run 2H	Run 2I	Average	Run 10G	Run 10H	Run 10I	Average	Run 18G	Run 18H	Run 18I	Average	Std. dev.	Mean	Low	High
Naphthalene	0.48	0.42	0.55	0.49	0.60	0.51	0.78	0.63	0.37	0.34	0.32	0.34	0.15	0.49	0.21	0.77
Acenaphthalene	0.61	0.65	0.66	0.64	0.55	0.59	0.61	0.59	0.66	0.71	0.70	0.69	0.05	0.64	0.54	0.74
Acenaphthene	22.23	23.43	21.68	22.44	24.39	23.58	21.79	23.26	20.06	23.27	21.57	21.63	1.34	22.44	19.89	24.99
Fluorene	20.10	20.44	19.42	19.99	20.25	20.09	19.79	20.04	19.95	20.79	19.04	19.93	0.53	19.99	18.98	20.99
Phenanthrene	25.52	26.30	26.08	25.97	23.47	23.20	24.73	23.80	27.58	29.39	27.44	28.14	2.01	25.97	22.13	29.80
Anthracene	1.65	0.73	0.86	1.08	1.84	0.00	1.72	1.19	1.46	1.46	0.00	0.97	0.72	1.08	-0.29	2.45
Fluoranthene	9.70	10.57	10.08	10.11	9.04	9.13	9.74	9.30	10.36	12.00	10.41	10.92	0.89	10.11	8.41	11.82
Pyrene	2.84	3.05	3.03	2.97	2.68	2.65	2.98	2.77	3.01	3.44	3.08	3.18	0.24	2.97	2.52	3.43
Benz(a)anthracene	0.24	0.19	0.28	0.24	0.32	0.24	0.31	0.29	0.17	0.14	0.24	0.18	0.06	0.24	0.12	0.35
Chrysene	0.28	0.32	0.34	0.31	0.26	0.31	0.36	0.31	0.30	0.33	0.32	0.32	0.03	0.31	0.25	0.37
Benzo(b)fluoranthene	0.50	0.41	0.48	0.46	0.67	0.43	0.51	0.54	0.33	0.38	0.46	0.39	0.10	0.46	0.28	0.65
Benzo(k)fluoranthene	0.50	0.41	0.48	0.46	0.67	0.43	0.51	0.54	0.33	0.39	0.46	0.39	0.10	0.46	0.28	0.65
Benzo(a)pyrene	0.15	0.08	0.13	0.12	0.21	0.10	0.11	0.14	0.09	0.05	0.15	0.10	0.05	0.12	0.03	0.21
Indeno(1,2,3-c,d)pyrene	nd	nd	nd	nd	0.05	nd	nd	0.05	nd	nd	nd	nd				
Dibenz(a,h)anthracene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd				
Benzo(g,h,i)perylene	nd	nd	nd	nd	nd	0.03	nd	0.03	nd	nd	0.03	0.03				
Totals	84.80	86.98	84.07	85.28	84.99	81.30	83.94	83.41	84.67	92.69	84.23	87.20	3.14	85.30	79.31	91.29

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Values enclosed in a box fall outside Chauvignot's Range by a marginal amount, therefore, these data points are accepted.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 5, 13, & 21: Moisture content is HIGH and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

															Chauvignot's Range Data points=9	
PAH compound	Run 5A	Run 5B	Run 5C	Average	Run 13A	Run 13B	Run 13C	Average	Run 21A	Run 21B	Run 21C	Average	Std. dev.	Mean	Low	High
Naphthalene	0.32	0.26	1.08	0.55	0.21	0.24	0.32	0.26	0.22	0.20	0.24	0.22	0.28	0.34	-0.18	0.86
Acenaphthalene	0.45	0.52	0.54	0.50	0.53	0.59	0.63	0.58	0.50	0.58	0.53	0.54	0.05	0.54	0.44	0.64
Acenaphthene	20.95	20.77	22.85	21.52	23.07	25.13	25.78	24.66	21.30	22.92	22.12	22.11	1.76	22.77	19.41	26.12
Fluorene	17.60	18.92	19.43	18.65	19.51	21.16	21.35	20.67	17.64	19.76	18.96	18.79	1.31	19.37	16.86	21.88
Phenanthrene	23.80	25.70	25.97	25.16	24.14	24.65	25.15	24.65	23.59	27.18	26.09	25.62	1.20	25.14	22.85	27.43
Anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.06	0.35	0.35	0.12	-0.56	0.79
Fluoranthene	11.09	10.78	10.87	10.91	10.67	12.05	13.03	11.92	9.69	11.59	10.53	10.60	0.97	11.14	9.29	12.99
Pyrene	2.26	2.38	2.32	2.32	2.42	2.98	3.10	2.83	2.45	2.99	2.61	2.68	0.32	2.61	1.99	3.23
Benz(a)anthracene	0.07	0.03	0.05	0.05	0.08	0.04	0.04	0.05	0.09	0.03	0.06	0.06	0.02	0.06	0.01	0.10
Chrysene	0.32	0.34	0.27	0.31	0.28	0.41	0.42	0.37	0.00	0.20	0.19	0.13	0.13	0.27	0.02	0.52
Benzo(b)fluoranthene	0.40	0.20	0.30	0.30	0.30	0.43	0.38	0.37	0.87	0.34	nd	0.61	0.20	0.40	0.01	0.79
Benzo(k)fluoranthene	0.40	0.22	0.30	0.31	0.30	0.41	0.38	0.36	0.87	0.33	nd	0.60	0.20	0.40	0.02	0.79
Benzo(a)pyrene	0.02	nd	0.03	0.02	nd	0.02	nd		0.17	nd	nd	0.17	0.07	0.06	-0.08	0.20
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	77.68	80.14	84.01	80.61	81.51	88.10	90.57	86.73	77.40	86.11	82.38	81.97	4.53	83.10	74.44	91.76

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 5, 13, & 21: Moisture content is HIGH and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

D,E,F SERIES: TOP OF CELL AFTER FREEZING

															Chauvignot's Range	
													Standard		Data points=9	
PAH compound	Run 5D	Run 5E	Run 5F	Avgs.	Run 13D	Run 13E	Run 13F	Avgs.	Run 21D	Run 21E	Run 21F	Avgs.	Deviation	Mean	Low	High
Naphthalene	0.26	0.23	0.23	0.24	0.25	0.21	0.33	0.26	0.27	0.31	0.27	0.28	0.04	0.26	0.18	0.34
Acenaphthalene	0.62	0.57	0.58	0.59	0.72	0.71	$\boxed{0.83}$	0.75	0.66	0.63	0.60	0.63	0.08	0.66	0.50	0.82
Acenaphthene	26.35	23.77	26.78	25.63	25.78	27.37	30.02	27.72	28.71	28.48	28.07	28.42	1.85	27.26	23.73	30.79
Fluorene	21.45	20.61	21.62	21.23	20.22	21.91	23.53	21.89	25.28	24.64	24.41	24.78	1.87	22.63	19.07	26.19
Phenanthrene	24.41	21.82	22.46	22.89	22.79	26.33	26.05	25.06	37.86	33.47	34.06	35.13	5.90	27.70	16.43	38.97
Anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fluoranthene	11.09	8.10	9.47	9.56	9.38	11.64	11.19	10.74	15.94	14.31	15.11	15.12	2.74	11.80	6.56	17.04
Pyrene	2.81	1.90	2.26	2.32	2.85	3.67	4.33	3.62	4.45	3.88	4.00	4.11	0.92	3.35	1.59	5.11
Benz(a)anthracene	0.06	0.04	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01	0.02	0.02	-0.03	0.06
Chrysene	0.21	0.18	0.26	0.22	0.25	0.47	$\boxed{0.57}$	0.43	0.26	0.18	0.28	0.24	0.14	0.30	0.04	0.55
Benzo(b)fluoranthene	0.37	0.21	0.26	0.28	0.32	nd	0.41	0.36	0.51	0.40	0.48	0.47	0.10	0.37	0.17	0.57
Benzo(k)fluoranthene	0.37	0.00	0.26	0.21	0.28	nd	nd	0.28	0.27	0.40	0.48	0.39	0.15	0.30	0.01	0.59
Benzo(a)pyrene	0.06	nd	nd		nd	nd	nd		nd	nd	nd					
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	88.06	77.43	84.21	83.23	82.85	92.32	97.27	90.81	114.21	106.71	107.79	109.57	12.75	94.54	70.18	118.89

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Values enclosed in a box denote values which are outside Chauvignot's Range, but close enough to the range to be acceptable.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 5, 13, & 21: Moisture content is HIGH and the Freezing Rate is SLOW

CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

G,H,I SERIES: BOTTOM OF CELL AFTER FREEZING

PAH compound	Run 5G	Run 5H	Runs 5I	Average	Run 13G	Run 13H	Run 13I	Average	Run 21G	Run 21H	Run 21I	Average	Standard Deviation	Mean	Chauvignot's Range Data points=9 Low	High
Naphthalene	0.47	0.36		0.41	0.27	0.26	0.38	0.30	0.31	0.23	0.33	0.29	0.08	0.32	0.18	0.47
Acenaphthalene	0.57	0.58		0.57	0.72	0.79	0.81	0.77	0.60	0.65	0.58	0.61	0.10	0.66	0.48	0.85
Acenaphthene	24.91	24.90	GC	24.91	28.82	28.10	28.65	28.52	24.33	26.57	25.37	25.42	1.84	26.46	23.04	29.88
Fluorene	20.11	20.48		20.29	21.54	22.77	21.92	22.08	20.20	22.77	22.56	21.84	1.15	21.54	19.41	23.68
Phenanthrene	20.70	24.04	vial	22.37	23.36	27.71	25.78	25.62	26.24	31.53	31.75	29.84	3.86	26.39	19.21	33.57
Anthracene	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fluoranthene	8.00	10.66	broke	9.33	11.01	12.60	10.58	11.40	9.14	11.99	13.97	11.70	1.90	10.99	7.47	14.52
Pyrene	2.01	2.68		2.35	3.66	4.75	3.84	4.08	2.46	3.37	3.77	3.20	0.89	3.32	1.67	4.97
Benz(a)anthracene	0.04	$\boxed{0.11}$		0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.02	-0.05	0.09
Chrysene	0.26	0.29		0.28	0.54	0.64	0.55	0.58	0.18	0.24	0.32	0.24	0.17	0.38	0.05	0.70
Benzo(b)fluoranthene	0.21	0.37		0.29	nd	0.49	nd	0.49	0.00	0.32	0.49	0.27	0.19	0.31	-0.03	0.66
Benzo(k)fluoranthene	0.21	0.37		0.29	nd	0.48	nd	0.48	0.16	0.36	0.43	0.32	0.13	0.34	0.10	0.57
Benzo(a)pyrene	nd	0.08		0.08	nd	nd	nd		nd	nd	nd					
Indeno(1,2,3-c,d)pyrene	nd	nd			nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd			nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd			nd	nd	nd		nd	nd	nd					
Totals	77.48	84.92		81.20	89.91	98.61	92.51	93.68	83.61	98.03	99.57	93.74	8.08	90.58	75.55	105.61

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Values enclosed in a box denote values which are outside Chauvignot's Range, but close enough to the range to be acceptable.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 6, 14, & 22: Moisture content is HIGH and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

															Chauvignot's Rang	
															Data points=9	
PAH compound	Run 6A	Run 6B	Run 6C	Avgs.	Run 14A	Run 14B	Run 14C	Avgs.	Run 22A	Run 22B	Run 22C	Avgs.	Std. dev.	Mean	Low	High
Naphthalene	0.25	0.22	0.24	0.24	0.36	0.23	0.37	0.32	0.15	0.00	0.21	0.12	0.11	0.23	0.01	0.44
Acenaphthalene	0.55	0.57	0.61	0.58	0.88	0.90	0.92	0.90	0.89	0.91	0.97	0.92	0.17	0.80	0.47	1.13
Acenaphthene	24.76	23.65	24.53	24.31	21.48	22.63	23.58	22.57	24.98	24.55	24.67	24.73	1.17	23.87	21.64	26.10
Fluorene	21.03	19.97	20.84	20.61	19.47	18.58	20.42	19.49	21.15	21.44	21.23	21.27	0.95	20.46	18.64	22.28
Phenanthrene	28.53	27.47	27.02	27.67	24.18	22.06	26.60	24.28	27.03	25.73	25.11	25.96	1.96	25.97	22.23	29.71
Anthracene	nd	nd	nd		1.45	0.57	0.21	0.74	nd	nd	nd		0.64	0.74	-0.47	1.96
Fluoranthene	10.49	10.52	11.24	10.75	8.41	6.69	10.24	8.45	10.10	10.58	11.28	10.65	1.48	9.95	7.12	12.78
Pyrene	2.76	2.83	3.22	2.94	2.45	2.00	3.19	2.55	3.05	3.70	3.48	3.41	0.52	2.97	1.97	3.96
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.30	0.14	0.00	0.15	0.00	0.00	0.00	0.00	0.10	0.05	-0.15	0.25
Chrysene	0.21	0.21	0.20	0.21	0.00	0.00	0.14	0.05	0.22	0.32	0.30	0.28	0.11	0.18	-0.04	0.39
Benzo(b)fluoranthene	0.22	nd	0.00	0.11	0.00	nd	0.23	0.11	nd	nd	nd		0.13	0.11	-0.14	0.36
Benzo(k)fluoranthene	0.22	nd	0.27	0.24	0.18	nd	0.23	0.21	nd	nd	nd		0.04	0.23	0.15	0.30
Benzo(a)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	89.03	85.42	88.16	87.54	79.17	73.81	86.15	79.71	87.57	87.22	87.27	87.35	5.04	84.87	75.23	94.50

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 6, 14, & 22: Moisture content is HIGH and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

D,E,F SERIES: TOP OF CELL AFTER FREEZING

															Chauvignot's range Data points=9	
PAH compound	Run 6D	Run 6E	Run 6F	Average	Run 14D	Run 14E	Run 14F	Average	Run 22D	Run 22E	Run 22F	Average	Std. dev.	Mean	Low	High
Naphthalene	0.23	0.30	0.31	0.28	0.28	0.32	0.32	0.31	0.22	0.31	0.26	0.26	0.04	0.28	0.21	0.36
Acenaphthalene	0.56	0.56	0.61	0.58	1.00	1.07	1.12	1.06	0.93	0.93	0.90	0.92	0.22	0.85	0.43	1.27
Acenaphthene	22.56	24.00	25.29	23.95	25.84	27.10	27.97	26.97	27.10	27.21	27.01	27.11	1.77	26.01	22.63	29.39
Fluorene	19.11	18.77	19.83	19.24	21.96	24.48	25.23	23.89	23.34	23.74	23.15	23.41	2.40	22.18	17.60	26.75
Phenanthrene	25.06	25.72	27.17	25.98	29.96	32.44	34.13	32.18	31.33	31.25	28.78	30.45	3.10	29.54	23.63	35.45
Anthracene	0.00	0.00	0.00	0.00	0.87	0.18	0.85	0.63	0.00	0.00	0.00	0.00	0.37	0.21	-0.50	0.92
Fluoranthene	9.29	9.88	9.93	9.70	10.27	11.47	12.61	11.45	13.20	14.19	12.19	13.19	1.71	11.45	8.19	14.71
Pyrene	2.49	2.62	2.67	2.59	3.30	3.89	4.26	3.82	4.41	4.55	4.09	4.35	0.83	3.59	2.01	5.16
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chrysene	0.17	0.20	0.00	0.12	0.05	0.00	0.00	0.02	0.33	0.38	0.38	0.36	0.16	0.17	-0.15	0.48
Benzo(b)fluoranthene	nd	nd	nd		0.22	0.29	0.35	0.29	nd	0.41	nd	0.41	0.08	0.32	0.16	0.48
Benzo(k)fluoranthene	nd	nd	nd		0.22	0.35	0.35	0.31	nd	nd	nd		0.08	0.31	0.16	0.45
Benzo(a)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	79.47	82.05	85.82	82.44	93.94	101.59	107.18	100.90	100.86	102.98	96.75	100.19	9.91	94.51	75.59	113.43

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR CLAY SOIL

RUNS 6, 14, & 22: Moisture content is HIGH and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

G,H,I SETIES: BOTTOM OF CELL AFTER FREEZING

															Chauvignot's range	
															Data points=9	
PAH compound	Run 6G	Run 6H	Run 6I	Avgs.	Run 14G	Run 14H	Run 14I	Avgs.	Run 22G	Run 22H	Run 22I	Avgs.	Std. dev.	Mean	Low	High
Naphthalene	0.21	0.37	0.30	0.29	0.61	0.38	0.30	0.43	0.22	0.31	0.15	0.23	0.13	0.32	0.06	0.57
Acenaphthalene	0.53	0.62	0.52	0.56	1.00	1.01	1.03	1.01	0.88	0.92	0.92	0.91	0.21	0.82	0.42	1.23
Acenaphthene	20.51	25.70	23.59	23.26	23.87	27.63	27.24	26.25	23.96	24.23	24.45	24.21	2.13	24.57	20.51	28.64
Fluorene	18.25	21.42	18.45	19.37	21.52	24.31	23.52	23.12	19.53	20.81	20.94	20.42	2.06	20.97	17.03	24.91
Phenanthrene	24.91	30.32	24.40	26.54	28.09	31.62	29.21	29.64	24.43	26.73	26.47	25.87	2.63	27.35	22.32	32.38
Anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Fluoranthene	10.28	11.93	8.70	10.30	10.24	13.76	11.52	11.84	9.66	10.60	12.18	10.81	1.52	10.99	8.08	13.89
Pyrene	2.75	3.19	2.29	2.74	3.41	4.61	3.93	3.98	3.23	3.62	4.09	3.65	0.70	3.46	2.12	4.80
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chrysene	0.18	0.26	0.18	0.21	0.29	0.34	0.25	0.29	0.29	0.36	0.35	0.33	0.07	0.28	0.15	0.41
Benzo(b)fluoranthene	0.23	0.32	nd	0.28	nd	0.41	nd	0.41	nd	nd	nd		0.09	0.32	0.15	0.49
Benzo(k)fluoranthene	0.22	0.31	nd	0.27	nd	0.41	nd	0.41	nd	nd	nd		0.09	0.31	0.13	0.49
Benzo(a)pyrene	nd	0.03	nd	0.03	nd	nd	nd		nd	nd	nd					
Indeno(1,2,3-c,d)pyrene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Dibenz(a,h)anthracene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Benzo(g,h,i)perylene	nd	nd	nd		nd	nd	nd		nd	nd	nd					
Totals	78.06	94.47	78.42	83.65	89.03	104.47	97.01	96.84	82.19	87.59	89.55	86.44	8.76	88.98	72.25	105.70

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Appendix A-2. Raw Data for High Level Contaminated Sand Soil

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 3, 11, & 19: Moisture content is LOW and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

															Chauvignot's range Data points=9	
PAH compound	Run 3A	Run 3B	Run 3C	Average	Run 11A	Run 11B	Run 11C	Average	Run 19A	Run19B	Run19C	Average	Standard Deviation	Mean	Low	High
Naphthalene	7.30	7.50	7.40	7.40	6.10	6.10	5.90	6.03	3.60	3.35	3.70	3.55	1.69	5.66	2.42	8.90
Acenaphthalene	0.20	0.30	0.30	0.27	0.20	0.20	0.20	0.20	0.40	0.20	0.20	0.27	0.07	0.24	0.11	0.38
Acenaphthene	8.10	8.10	7.50	7.90	7.60	7.00	7.40	7.33	8.50	8.40	8.70	8.53	0.57	7.92	6.83	9.02
Fluorene	7.00	6.70	6.10	6.60	6.50	5.60	6.10	6.07	7.20	7.10	7.30	7.20	0.59	6.62	5.50	7.75
Phenanthrene	16.30	16.20	14.00	15.50	15.50	12.10	14.70	14.10	16.50	16.50	17.50	16.83	1.64	15.48	12.34	18.61
Anthracene	2.60	2.30	2.00	2.30	2.30	1.80	2.10	2.07	2.60	3.80	4.00	3.47	0.78	2.61	1.13	4.10
Fluoranthene	10.10	10.10	8.00	9.40	11.00	7.30	10.00	9.43	13.00	12.35	13.10	12.82	2.05	10.55	6.63	14.47
Pyrene	3.50	3.20	2.70	3.13	3.60	2.40	3.60	3.20	4.70	4.45	4.70	4.62	0.83	3.65	2.06	5.24
Benz(a)anthracene	1.20	1.00	0.80	1.00	1.10	0.70	1.00	0.93	1.40	1.20	1.30	1.30	0.23	1.08	0.64	1.51
Chrysene	1.10	1.00	0.80	0.97	1.10	0.70	1.00	0.93	1.40	1.20	1.30	1.30	0.22	1.07	0.64	1.49
Benzo(b+k)fluoranthene	0.70	0.70	0.50	0.63	0.80	0.50	0.70	0.67	1.20	1.20	1.20	1.20	0.29	0.83	0.28	1.39
Benzo(a)pyrene	0.30	0.30	0.20	0.27	0.30	0.20	0.30	0.27	0.50	0.35	0.40	0.42	0.09	0.32	0.14	0.50
Indeno(1,2,3-c,d)pyrene	0.10	0.10	0.00	0.07	0.10	0.00	0.10	0.07	0.10	0.10	0.10	0.10	0.04	0.08	-0.01	0.16
Dibenz(a,h)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	0.10	0.10	0.00	0.07	0.10	0.00	0.10	0.07	0.10	0.05	0.10	0.08	0.04	0.07	-0.01	0.16
Totals	58.60	57.60	50.30	55.50	56.30	44.60	53.20	51.37	61.20	60.25	63.60	61.68	5.94	56.18	44.84	67.53

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Values enclosed in a box fall outside Chauvignot's range, but are sufficiently close to the range to be acceptable.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 3, 11, & 19: Moisture content is LOW and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

D,E,F SERIES: TOP OF CELL AFTER FREEZING

															Chauvignot's range	
															Data points=9	
PAH compound	Run 3D	Run 3E	Run 3F	Avgs.	Run 11D	Run 11E	Run11F	Avgs.	Run19D	Run19E	Run19F	Avgs.	Std. dev.	Mean	Low	High
Naphthalene	7.00	7.80	7.40	7.40	6.10	5.60	5.90	5.87	4.40	5.00	5.10	4.83	1.16	6.03	3.82	8.25
Acenaphthalene	0.14	nd	nd	0.14	0.20	0.20	0.20	0.20	0.30	0.20	0.20	0.23	0.05	0.21	0.12	0.30
Acenaphthene	6.50	7.40	7.30	7.07	7.00	7.10	6.90	7.00	6.00	7.90	9.10	7.67	0.88	7.24	5.56	8.93
Fluorene	5.70	6.80	6.70	6.40	5.90	5.90	5.80	5.87	4.80	6.30	7.30	6.13	0.74	6.13	4.73	7.54
Phenanthrene	12.60	15.50	14.80	14.30	13.10	13.20	13.00	13.10	9.90	13.10	15.80	12.93	1.78	13.44	10.04	16.85
Anthracene	1.50	1.80	1.80	1.70	2.00	2.00	2.00	2.00	1.50	2.00	3.80	2.43	0.69	2.04	0.73	3.36
Fluoranthene	6.80	8.30	8.20	7.77	7.60	8.00	7.40	7.67	6.50	8.60	10.20	8.43	1.09	7.96	5.87	10.04
Pyrene	2.50	2.90	2.60	2.67	3.30	3.10	2.80	3.07	2.30	3.10	3.60	3.00	0.41	2.91	2.13	3.70
Benz(a)anthracene	0.60	0.80	0.80	0.73	0.90	0.90	0.80	0.87	0.60	0.80	0.90	0.77	0.12	0.79	0.57	1.01
Chrysene	0.70	0.80	0.80	0.77	0.80	0.90	0.80	0.83	0.60	0.80	0.90	0.77	0.09	0.79	0.61	0.97
Benzo(b+k)fluoranthene	0.50	0.60	0.60	0.57	0.60	0.60	0.60	0.60	0.50	0.80	0.70	0.67	0.09	0.61	0.43	0.79
Benzo(a)pyrene	0.20	0.20	0.30	0.23	0.20	0.20	0.20	0.20	0.20	0.30	0.20	0.23	0.04	0.22	0.14	0.31
Indeno(1,2,3-c,d)pyrene	0.00	0.10	0.10	0.07	0.00	0.10	0.00	0.03	0.00	0.00	0.00	0.00	0.05	0.03	-0.06	0.13
Dibenz(a,h)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	0.00	0.10	0.10	0.07	0.00	0.10	0.00	0.03	0.00	0.00	0.00	0.00	0.05	0.03	-0.06	0.13
Totals	44.74	53.10	51.50	49.78	47.70	47.90	46.40	47.33	37.60	48.90	57.80	48.10	5.65	48.40	37.62	59.19

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

Values enclosed in a box fall outside Chauvignot's range, but are sufficiently close to the range to be acceptable.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 3, 11, & 19: Moisture content is LOW and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

G,H,I SERIES: BOTTOM OF CELL AFTER FREEZING

															Chauvignot's range Data points=9	
PAH compound	Run 3G	Run 3H	Run 3I	Avgs.	Run 11G	Run 11 H	Run 11 I	Avgs.	Run 19G	Run19H	Run19I	Avgs.	Std. dev.	Mean	Low	High
Naphthalene	7.40	7.60	6.90	7.30	5.30	5.60	5.90	5.60	3.60	3.90	4.80	4.10	1.44	5.67	2.92	8.42
Acenaphthalene	0.00	0.00	0.00	0.00	0.20	0.20	0.20	0.20	0.40	0.20	0.30	0.30	0.14	0.17	-0.10	0.44
Acenaphthene	6.30	6.70	6.10	6.37	6.40	6.90	6.70	6.67	7.20	7.80	12.20	9.07	1.88	7.37	3.77	10.96
Fluorene	5.10	6.00	5.30	5.47	5.80	6.30	6.10	6.07	6.10	6.40	10.80	7.77	1.69	6.43	3.20	9.67
Phenanthrene	10.90	12.20	11.00	11.37	13.00	14.70	14.00	13.90	15.00	15.50	nd	15.25	1.79	13.29	9.86	16.71
Anthracene	1.30	1.50	1.30	1.37	1.90	2.00	2.20	2.03	3.50	3.70	3.20	3.47	0.94	2.29	0.49	4.09
Fluoranthene	4.90	6.00	5.30	5.40	7.80	9.10	8.50	8.47	11.70	11.40	19.20	14.10	4.44	9.32	0.85	17.79
Pyrene	1.60	2.00	1.70	1.77	3.00	3.70	3.30	3.33	4.30	4.10	7.20	5.20	1.73	3.43	0.12	6.75
Benz(a)anthracene	0.40	0.50	0.40	0.43	0.90	1.00	1.00	0.97	1.20	1.10	nd	1.15	0.33	0.81	0.19	1.44
Chrysene	0.40	0.50	0.50	0.47	0.80	1.00	0.90	0.90	1.20	1.10	0.30	0.87	0.33	0.74	0.12	1.37
Benzo(b+k)fluoranthene	0.30	0.30	0.30	0.30	0.70	0.90	0.80	0.80	1.10	1.10	1.20	1.13	0.37	0.74	0.04	1.45
Benzo(a)pyrene	0.10	0.10	0.10	0.10	0.30	0.30	0.30	0.30	0.40	0.40	0.50	0.43	0.15	0.28	-0.01	0.56
Indeno(1,2,3-c,d)pyrene	0.00	0.00	0.00	0.00	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.05	0.07	-0.03	0.16
Dibenz(a,h)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.03	0.10	0.10	0.10	0.10	0.05	0.04	-0.06	0.15
Totals	38.70	43.40	38.90	40.33	46.20	51.90	50.00	49.37	55.90	56.90	59.90	57.57	7.79	49.09	34.21	63.97

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 4, 12, & 20: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

														Chauvignot's Range Data points=9	
PAH compound	Run4A	Run 4B	Run 4C	Avg.	Run12A	Run 12B	Run 12C	Avgs.	Run 20A	Run20B	Run20C	Avgs.	Std. dev.	Mean	Low	High
Naphthalene	8.20	8.90	7.90	8.33	5.30	5.20	5.10	5.20	2.02	1.90	1.80	1.91	2.79	5.15	-0.19	10.49
Acenaphthalene	0.20	0.30	0.20	0.23	0.10	0.10	nd	0.10	0.26	0.23	0.27	0.25	0.07	0.21	0.06	0.35
Acenaphthene	7.10	9.10	7.00	7.73	6.50	6.50	6.70	6.57	10.06	8.02	9.76	9.28	1.43	7.86	5.13	10.59
Fluorene	5.50	9.00	5.70	6.73	5.50	5.50	5.90	5.63	9.31	5.83	7.64	7.59	1.57	6.65	3.66	9.65
Phenanthrene	13.60	24.00	11.70	16.43	11.50	10.70	11.40	11.20	25.54	10.76	14.85	17.05	5.77	14.90	3.87	25.92
Anthracene	1.80	3.30	1.50	2.20	1.90	1.30	1.50	1.57	4.52	1.64	2.52	2.90	1.06	2.22	0.19	4.25
Fluoranthene	6.80	16.00	5.80	9.53	6.40	5.60	6.20	6.07	22.64	7.58	11.65	13.96	5.90	9.85	-1.43	21.13
Pyrene	2.20	5.40	2.00	3.20	2.10	2.00	2.10	2.07	6.36	3.15	4.75	4.75	1.71	3.34	0.08	6.60
Benz(a)anthracene	0.70	1.90	0.60	1.07	0.60	0.50	0.50	0.53	2.19	0.75	1.25	1.40	0.64	1.00	-0.22	2.22
Chrysene	0.70	1.80	0.50	1.00	0.60	0.50	0.50	0.53	1.97	0.44	1.06	1.16	0.59	0.90	-0.24	2.03
Benzo(b+k)fluoranthene	0.50	1.30	0.30	0.70	0.20	0.30	0.30	0.27	1.96	0.59	0.92	1.16	0.59	0.71	-0.42	1.83
Benzo(a)pyrene	0.20	0.50	0.10	0.27	0.20	0.10	0.10	0.13	0.49	0.14	0.24	0.29	0.16	0.23	-0.07	0.53
Indeno(1,2,3-c,d)pyrene	0.10	0.10	nd	0.10	nd	nd	nd	nd	0.20	0.04	0.08	0.11	0.06	0.11	-0.01	0.22
Dibenz(a,h)anthracene	nd	0.10	nd	0.10	nd	nd	nd	nd	0.08	0.02	0.03	0.04	0.04	0.06	-0.02	0.13
Benzo(g,h,i)perylene	0.10	0.20	nd	0.15	nd	nd	nd	nd	0.20	0.05	0.08	0.11	0.07	0.13	-0.01	0.26
Totals	47.70	81.90	43.30	57.63	40.90	38.30	40.30	39.83	87.82	41.14	56.92	61.96	18.87	53.14	17.09	89.19

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 4, 12, & 20: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

PAH compound	Run4D	Run4E	Run4F	Average	Run12D	Run 12E	Run12F	Average	Run20D	Run20E	Run20F	Average	Standard Deviation	Mean	Chauvignot's Range	
															Data points=9	
Naphthalene	8.20	7.50	7.90	7.87	5.60	5.70	5.80	5.70	2.21	1.89	1.61	1.90	2.63	5.16	0.14	10.17
Acenaphthalene	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.31	0.24	0.31	0.28	0.05	0.23	0.14	0.32
Acenaphthene	6.90	6.30	7.30	6.83	8.10	7.80	8.20	8.03	10.61	8.28	10.73	9.87	1.52	8.25	5.34	11.15
Fluorene	5.70	4.60	5.80	5.37	6.90	6.30	6.30	6.50	8.70	6.30	8.84	7.95	1.38	6.60	3.97	9.24
Phenanthrene	11.80	10.20	11.70	11.23	15.70	14.50	15.70	15.30	18.09	12.34	17.69	16.04	2.81	14.19	8.82	19.57
Anthracene	1.30	1.20	1.40	1.30	1.90	1.80	1.90	1.87	3.13	1.97	2.76	2.62	0.65	1.93	0.69	3.17
Fluoranthene	4.80	4.10	4.90	4.60	10.10	9.10	10.20	9.80	15.84	9.29	15.51	13.54	4.32	9.31	1.06	17.57
Pyrene	1.60	1.30	1.80	1.57	3.50	3.10	3.10	3.23	6.52	3.49	7.07	5.70	2.05	3.50	-0.41	7.41
Benz(a)anthracene	0.40	0.30	0.40	0.37	1.00	0.80	1.00	0.93	1.83	0.91	1.84	1.52	0.57	0.94	-0.15	2.03
Chrysene	0.40	0.30	0.40	0.37	1.00	0.90	1.00	0.97	1.51	0.76	1.53	1.27	0.46	0.87	0.00	1.74
Benzo(b+k)fluoranthene	0.20	0.20	0.20	0.20	0.50	0.40	0.60	0.50	1.42	0.71	1.50	1.21	0.50	0.64	-0.32	1.60
Benzo(a)pyrene	0.10	0.10	0.10	0.10	0.20	0.20	0.30	0.23	0.39	0.18	0.40	0.33	0.12	0.22	-0.01	0.45
Indeno(1,2,3-c,d)pyrene	0.00	0.10	0.00	0.03	0.10	0.10	0.10	0.10	0.13	0.06	0.13	0.10	0.05	0.08	-0.02	0.17
Dibenz(a,h)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.02	0.05	0.04	0.02	0.01	-0.03	0.06
Benzo(g,h,i)perylene	0.00	0.10	0.00	0.03	0.10	0.10	0.10	0.10	0.13	0.06	0.12	0.10	0.05	0.08	-0.02	0.17
Totals	41.60	36.50	42.10	40.07	54.90	51.00	54.50	53.47	70.87	46.50	70.09	62.49	12.12	52.01	28.85	75.16

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 4, 12, & 20: Moisture content is LOW and the Freezing Rate is FAST
VALUES REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

													Standard		Chauvignot's Range Data points=9	
PAH compound	Run4G	Run4H	Run4I	Average	Run 12G	Run 12 H	Run 12 I	Average	Run20G	Run20H	Run20I	Average	deviation	Mean	Low	High
Naphthalene	7.50	7.30	7.50	7.43	5.50	5.10	4.90	5.17	1.57	1.37	1.51	1.48	2.61	4.69	-0.28	9.67
Acenaphthalene	0.20	0.20	0.20	0.20	0.20	0.10	0.10	0.13	0.28	0.27	0.29	0.28	0.07	0.20	0.07	0.34
Acenaphthene	7.50	6.80	7.40	7.23	7.20	6.60	6.80	6.87	9.86	9.64	9.46	9.65	1.34	7.92	5.36	10.47
Fluorene	6.70	6.20	6.40	6.43	5.70	5.20	5.40	5.43	7.75	7.55	7.40	7.57	0.94	6.48	4.67	8.28
Phenanthrene	15.10	13.60	13.80	14.17	12.10	11.10	11.60	11.60	15.33	15.97	14.24	15.18	1.72	13.65	10.36	16.94
Anthracene	1.90	1.70	1.70	1.77	1.40	1.30	1.30	1.33	2.56	2.78	2.35	2.56	0.55	1.89	0.83	2.95
Fluoranthene	8.20	6.90	7.10	7.40	7.40	6.20	6.70	6.77	13.28	13.65	11.79	12.91	3.00	9.02	3.29	14.76
Pyrene	2.70	2.20	2.40	2.43	2.40	2.00	2.40	2.27	5.50	5.69	5.65	5.61	1.64	3.44	0.30	6.58
Benz(a)anthracene	0.80	0.60	0.70	0.70	0.70	0.50	0.60	0.60	1.50	1.54	1.34	1.46	0.42	0.92	0.12	1.72
Chrysene	0.80	0.60	0.70	0.70	0.70	0.60	0.70	0.67	0.74	1.27	0.71	0.91	0.20	0.76	0.37	1.14
Benzo(b+k)fluoranthene	0.40	0.40	0.40	0.40	0.40	0.30	0.40	0.37	1.16	1.26	1.03	1.15	0.39	0.64	-0.10	1.38
Benzo(a)pyrene	0.20	0.20	0.20	0.20	0.20	0.10	0.10	0.13	0.39	0.24	0.37	0.33	0.10	0.22	0.03	0.42
Indeno(1,2,3-c,d)pyrene	0.10	0.10	0.00	0.07	0.10	0.00	0.00	0.03	0.10	0.11	0.09	0.10	0.05	0.07	-0.03	0.16
Dibenz(a,h)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.04	0.04	0.04	0.02	0.01	-0.03	0.05
Benzo(g,h,i)perylene	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.09	0.10	0.01	0.10	0.09	0.11
Totals	52.20	46.90	48.60	49.23	44.10	39.20	41.10	41.47	60.16	61.50	56.37	59.35	8.09	50.02	34.57	65.46

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 7, 15, & 23: Moisture content is HIGH and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

															Chauvignot's range	
															Data points=9	
PAH compound	Run7A	Run7B	Run7C	Average	Run15A	Run15B	Run15C	Average	Run23A	Run23B	Run23C	Average	Standard Deviation	Mean	Low	High
Naphthalene	4.07	4.18	4.18	4.14	1.19	1.15	1.13	1.16	3.21	3.29	3.34	3.28	1.33	2.86	0.32	5.40
Acenaphthalene	0.16	0.18	0.16	0.17	0.21	0.19	0.19	0.20	0.24	0.22	0.23	0.23	0.03	0.20	0.15	0.25
Acenaphthene	6.58	7.02	6.55	6.72	8.26	7.45	7.82	7.84	9.28	8.69	8.88	8.95	1.01	7.84	5.91	9.77
Fluorene	5.08	5.65	5.25	5.33	6.89	6.27	6.75	6.64	7.69	7.19	7.28	7.39	0.94	6.45	4.66	8.24
Phenanthrene	8.20	7.92	9.46	8.53	14.63	13.52	15.40	14.52	17.73	15.25	14.83	15.94	3.55	12.99	6.21	19.77
Anthracene	0.98	1.29	1.04	1.10	2.03	2.04	2.58	2.22	2.85	2.40	2.28	2.51	0.69	1.94	0.63	3.25
Fluoranthene	5.74	6.72	6.09	6.18	13.63	12.75	15.09	13.82	14.90	11.16	10.88	12.31	3.74	10.77	3.64	17.91
Pyrene	1.96	2.21	1.91	2.02	4.23	3.48	4.01	3.91	3.42	2.75	2.70	2.95	0.86	2.96	1.31	4.61
Benz(a)anthracene	0.40	0.50	0.42	0.44	0.95	0.84	1.03	0.94	0.49	0.56	0.54	0.53	0.24	0.64	0.18	1.09
Chrysene	0.38	0.34	0.37	0.36	0.62	0.62	0.95	0.73	0.67	0.53	0.50	0.57	0.19	0.55	0.19	0.92
Benzo(b+k)fluoranthene	0.32	0.36	0.33	0.34	0.90	0.76	0.88	0.85	0.92	0.68	0.64	0.75	0.25	0.64	0.17	1.12
Benzo(a)pyrene	0.11	0.14	0.12	0.12	0.22	0.14	0.17	0.18	0.09	0.12	0.01	0.08	0.06	0.13	0.02	0.23
Indeno(1,2,3-c,d)pyrene	nd	0.01	0.02	0.01	0.06	0.01	0.01	0.03	nd	nd	nd	nd	0.02	0.02	-0.02	0.06
Dibenz(a,h)anthracene	nd	nd	nd	nd	0.03	0.01	0.01	0.02	nd	nd	nd	nd	0.01	0.02	-0.01	0.04
Benzo(g,h,i)perylene	0.01	nd	0.02	0.01	0.06	nd	nd	0.06	nd	nd	nd	nd	0.03	0.03	-0.02	0.08
Totals	34.00	36.51	35.90	35.47	53.91	49.23	56.02	53.05	61.49	52.85	52.12	55.49	9.99	48.00	28.93	67.08

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 7, 15, & 23: Moisture content is HIGH and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

															Chauvignot's range	
													Standard		Data points=9	
PAH compound	Run7D	Run7E	Run7F	Average	Run15D	Run15E	Run15F	Average	Run23D	Run23E	Run23F	Average	deviation	Mean	Low	High
Naphthalene	4.06	3.80	3.72	3.86	1.30	1.30	1.49	1.36	2.95	2.89	2.54	2.79	1.09	2.67	0.58	4.76
Acenaphthalene	0.18	0.16	0.15	0.17	0.19	0.18	0.23	0.20	0.22	0.22	0.20	0.22	0.03	0.19	0.14	0.24
Acenaphthene	7.33	6.76	6.38	6.83	8.18	7.46	9.26	8.30	8.37	8.40	7.97	8.24	0.89	7.79	6.08	9.50
Fluorene	6.12	5.45	5.21	5.60	6.65	5.93	7.44	6.67	6.66	6.97	6.43	6.68	0.71	6.32	4.96	7.68
Phenanthrene	11.99	10.14	9.76	10.63	14.24	12.22	16.40	14.29	14.70	14.39	13.38	14.15	2.19	13.03	8.84	17.21
Anthracene	1.36	1.09	0.92	1.12	2.56	2.17	2.18	2.30	2.23	2.32	1.95	2.17	0.59	1.86	0.74	2.99
Fluoranthene	8.39	6.50	6.33	7.07	13.49	12.18	14.19	13.29	10.83	10.27	9.45	10.18	2.82	10.18	4.80	15.56
Pyrene	2.65	2.10	1.94	2.23	3.36	2.62	3.60	3.19	2.55	2.74	2.51	2.60	0.53	2.67	1.66	3.69
Benz(a)anthracene	0.61	0.46	0.40	0.49	0.65	0.32	0.60	0.52	0.31	0.56	0.44	0.44	0.13	0.48	0.24	0.73
Chrysene	0.52	0.39	0.34	0.42	0.73	0.53	0.68	0.65	0.58	0.52	0.15	0.42	0.18	0.49	0.16	0.83
Benzo(b+k)fluoranthene	0.47	0.35	0.32	0.38	0.68	0.51	0.88	0.69	0.60	0.67	0.58	0.62	0.18	0.56	0.23	0.90
Benzo(a)pyrene	0.18	0.13	0.11	0.14	0.13	0.13	0.31	0.19	0.11	0.15	0.12	0.13	0.06	0.15	0.03	0.27
Indeno(1,2,3-c,d)pyrene	0.03	0.02	0.02	0.02	nd	nd	nd	nd	nd	0.08	nd	0.08	0.03	0.04	-0.01	0.09
Dibenz(a,h)anthracene	0.01	0.01	0.01	0.01	nd	nd	nd	nd	nd	0.01	nd	0.01	0.00	0.01	0.00	0.02
Benzo(g,h,i)perylene	0.02	0.02	0.02	0.02	nd	nd	nd	nd	nd	0.07	nd	0.07	0.03	0.03	-0.02	0.08
Totals	43.94	37.37	35.63	38.98	52.17	45.56	57.25	51.66	50.09	50.25	45.72	48.69	6.93	46.44	33.20	59.68

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 7, 15, & 23: Moisture content is HIGH and the Freezing Rate is SLOW
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

															Chauvignot's range Data points=9	
PAH compound	Run7G	Run7H	Run7I	Average	Run15G	Run15H	Run15I	Average	Run23G	Run23H	Run23I	Average	Standard Deviation	Mean	Low	High
Naphthalene	3.57	3.66	3.55	3.59	1.48	1.57	1.56	1.53	2.85	3.03	3.11	3.00	0.92	2.71	0.95	4.46
Acenaphthalene	0.15	0.15	0.14	0.15	0.21	0.24	0.23	0.23	0.22	0.21	0.23	0.22	0.04	0.20	0.12	0.27
Acenaphthene	6.21	5.95	5.80	5.99	8.51	8.90	8.85	8.75	8.47	8.00	8.85	8.44	1.34	7.73	5.17	10.28
Fluorene	5.11	4.78	4.62	4.84	6.77	6.98	6.91	6.89	6.84	6.54	7.50	6.96	1.08	6.23	4.16	8.30
Phenanthrene	9.84	8.75	8.46	9.02	14.12	14.59	13.85	14.19	15.72	14.34	12.85	14.30	2.74	12.50	7.26	17.74
Anthracene	1.09	0.87	0.75	0.90	2.04	2.22	2.08	2.11	2.45	2.15	2.36	2.32	0.67	1.78	0.49	3.06
Fluoranthene	6.57	5.38	5.37	5.78	12.42	11.94	11.65	12.00	13.90	10.59	12.94	12.47	3.37	10.08	3.65	16.52
Pyrene	2.16	1.73	1.69	1.86	2.88	2.83	2.77	2.83	3.12	2.78	3.27	3.06	0.58	2.58	1.48	3.69
Benz(a)anthracene	0.47	0.36	0.34	0.39	0.59	0.53	0.55	0.56	0.41	0.51	0.16	0.36	0.14	0.44	0.18	0.69
Chrysene	0.40	0.29	0.26	0.32	0.56	0.56	0.55	0.56	0.39	0.24	1.04	0.56	0.25	0.48	0.00	0.95
Benzo(b+k)fluoranthene	0.36	0.23	0.27	0.29	0.71	0.73	0.74	0.73	0.78	0.72	0.89	0.80	0.25	0.60	0.13	1.08
Benzo(a)pyrene	0.13	0.10	0.08	0.11	0.12	0.13	0.30	0.19	0.15	0.17	0.12	0.15	0.06	0.15	0.02	0.27
Indeno(1,2,3-c,d)pyrene	0.02	0.02	0.02	0.02	nd	nd	0.09	0.09	0.01	0.08	nd	0.04	0.04	0.04	-0.03	0.11
Dibenz(a,h)anthracene	0.01	0.01	nd	0.01	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i)perylene	0.02	0.02	0.02	0.02	nd	nd	0.09	0.09	nd	0.01	nd	0.01	0.04	0.03	-0.04	0.10
Totals	36.13	32.28	31.38	33.26	50.42	51.22	50.22	50.62	55.31	49.38	53.31	52.66	9.44	45.52	27.48	63.55

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 8, 16, & 24: Moisture content is HIGH and the Freezing Rate is FAST
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

A,B,C SERIES: BEFORE FREEZING, UNTREATED SOIL

													Standard		Chauvignot's range Data points=9	
PAH compound	Run8A	Run8B	Run8C	Average	Run16A	Run16B	Run16C	Average	Run24A	Run24B	Run24C	Average	Deviation	Mean	Low	High
Naphthalene	1.66	0.50	0.51	0.89	0.47	0.48	0.52	0.49	0.79	0.74	0.67	0.73	0.38	0.70	-0.02	1.43
Acenaphthalene	0.24	0.25	0.25	0.25	0.22	0.20	0.22	0.21	0.23	0.23	0.21	0.22	0.02	0.23	0.19	0.26
Acenaphthene	8.57	8.75	8.86	8.73	8.32	7.54	7.90	7.92	7.89	7.90	7.76	7.85	0.47	8.16	7.26	9.07
Fluorene	6.92	6.63	7.00	6.85	6.41	5.71	6.27	6.13	6.54	6.40	5.96	6.30	0.42	6.43	5.63	7.22
Phenanthrene	15.69	14.01	16.39	15.36	14.36	12.27	11.93	12.85	10.22	12.26	11.91	11.46	2.01	13.23	9.39	17.06
Anthracene	1.67	3.19	0.00	1.62	2.72	2.31	2.64	2.56	2.82	2.93	2.52	2.76	0.97	2.31	0.46	4.16
Fluoranthene	14.75	13.17	17.59	15.17	11.91	9.39	12.21	11.17	11.13	11.70	10.29	11.04	2.47	12.46	7.74	17.18
Pyrene	3.28	3.11	3.52	3.30	4.46	3.43	3.99	3.96	3.55	3.75	3.17	3.49	0.43	3.58	2.76	4.41
Benz(a)anthracene	0.47	0.32	0.46	0.42	1.29	0.92	1.16	1.12	1.05	1.13	0.89	1.03	0.35	0.86	0.18	1.53
Chrysene	0.65	0.56	0.70	0.64	1.07	0.45	0.76	0.76	0.89	0.44	0.59	0.64	0.21	0.68	0.29	1.07
Benzo(b+k)fluoranthene	0.88	0.79	0.94	0.87	0.91	0.69	0.93	0.84	0.90	0.95	0.77	0.87	0.09	0.86	0.69	1.03
Benzo(a)pyrene	0.23	0.18	0.19	0.20	0.30	0.23	0.30	0.28	0.24	0.14	0.17	0.18	0.06	0.22	0.11	0.33
Indeno(1,2,3-c,d)pyrene	nd	nd	nd	nd	0.09	0.06	0.10	0.08	0.09	0.09	0.07	0.08	0.01	0.08	0.06	0.11
Dibenz(a,h)anthracene	nd	nd	nd	nd	0.04	0.03	0.04	0.04	0.04	0.04	0.03	0.03	0.01	0.04	0.03	0.05
Benzo(g,h,i)perylene	nd	nd	nd	nd	0.10	0.07	0.09	0.09	0.09	0.09	0.07	0.08	0.01	0.08	0.06	0.11
Totals	55.01	51.46	56.41	54.29	52.68	43.77	49.07	48.50	46.47	48.78	45.08	46.78	4.38	49.86	41.50	58.21

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 8, 16, & 24: Moisture content is HIGH and the Freezing Rate is FAST
CONCENTRATIONS REPORTED IN THIS TABLE ARE μg of PAHs per gram of Dry Soil (μg/g)

													Standard		Chauvignot's range Data points=9	
PAH compound	Run 8D	Run8E	Run8F	Average	Run16D	Run16E	Run16F	Average	Run24D	Run24E	Run24F	Average	Deviation	Mean	Low	High
Naphthalene	0.48	0.49	0.49	0.49	0.65	0.67	0.59	0.64	0.70	0.72	0.67	0.70	0.10	0.61	0.42	0.79
Acenaphthalene	0.28	0.30	0.28	0.29	0.24	0.25	0.25	0.25	0.22	0.23	0.24	0.23	0.03	0.25	0.20	0.31
Acenaphthene	9.76	10.44	9.81	10.00	8.07	8.63	8.44	8.38	8.28	8.25	8.84	8.46	0.85	8.95	7.33	10.56
Fluorene	8.00	8.40	7.97	8.12	6.79	7.72	7.44	7.32	6.63	6.49	7.15	6.76	0.67	7.40	6.11	8.69
Phenanthrene	18.81	19.57	18.21	18.86	18.14	19.83	19.39	19.12	15.46	15.09	17.42	15.99	1.72	17.99	14.70	21.28
Anthracene	3.97	0.00	3.50	2.49	3.44	3.78	3.74	3.65	2.86	2.81	3.14	2.94	1.20	3.03	0.73	5.33
Fluoranthene	20.31	21.51	18.58	20.13	14.14	15.65	15.35	15.04	11.81	11.62	13.78	12.40	3.56	15.86	9.07	22.65
Pyrene	4.48	5.18	4.24	4.64	4.30	5.10	5.02	4.81	3.23	3.20	3.89	3.44	0.75	4.29	2.86	5.73
Benz(a)anthracene	0.81	1.17	0.89	0.96	1.37	1.65	1.60	1.54	1.01	1.02	1.22	1.08	0.30	1.19	0.63	1.76
Chrysene	0.99	1.16	0.85	1.00	0.92	1.44	0.88	1.08	0.37	0.84	0.84	0.68	0.29	0.92	0.38	1.47
Benzo(b+k)fluoranthene	1.29	1.53	1.20	1.34	1.11	1.41	1.36	1.30	0.84	0.85	1.01	0.90	0.25	1.18	0.71	1.65
Benzo(a)pyrene	0.41	0.29	0.00	0.23	0.48	0.60	0.30	0.46	0.26	0.15	0.27	0.23	0.18	0.31	-0.03	0.64
Indeno(1,2,3-c,d)pyrene	nd	nd	nd	nd	0.09	0.05	0.13	0.09	0.09	0.09	0.11	0.09	0.03	0.09	0.04	0.14
Dibenz(a,h)anthracene	nd	nd	nd	nd	0.04	0.04	0.06	0.05	0.03	0.04	0.04	0.04	0.01	0.04	0.03	0.06
Benzo(g,h,i)perylene	nd	nd	nd	nd	0.09	0.01	0.13	0.08	0.09	0.08	0.10	0.09	0.04	0.08	0.01	0.16
Totals	69.60	70.04	66.01	68.55	59.87	66.84	64.66	63.79	51.87	51.47	58.72	54.02	7.05	62.12	48.65	75.59

Note: shaded values fall outside Chauvignot's range of acceptable data. The normal probability plot is constructed as a check for acceptability of these values.

CONCENTRATION DATA OF THE 16 PRIORITY PAHs IN AQUEOUS PHASE FOR SAND SOIL

RUNS 8, 16, & 24: Moisture content is HIGH and the Freezing Rate is FAST
CONCENTRATIONS REPORTED IN THIS TABLE ARE µg of PAHs per gram of Dry Soil (µg/g)

G,H,I SERIES: BOTTOM OF CELL AFTER FREEZING

															Chauvignot's range Data points=9	
PAH compound	Run8G	Run8H	Run8I	Average	Run16G	Run16H	Run16I	Average	Run24G	Run24H	Run24I	Average	Standard Deviation	Mean	Low	High
Naphthalene	0.48	0.45	0.47	0.46	0.66	0.70	0.57	0.64	0.61	0.47	0.60	0.56	0.09	0.56	0.38	0.73
Acenaphthalene	0.19	0.18	0.22	0.19	0.27	0.23	0.24	0.25	0.27	0.23	0.21	0.24	0.03	0.23	0.16	0.29
Acenaphthene	7.43	7.21	8.47	7.71	9.06	7.52	7.88	8.15	9.20	7.97	7.59	8.25	0.72	8.04	6.66	9.41
Fluorene	5.54	5.35	6.50	5.80	8.13	6.51	6.58	7.07	7.65	6.44	6.14	6.74	0.89	6.54	4.84	8.24
Phenanthrene	11.88	11.15	14.16	12.39	21.54	16.01	16.77	18.11	19.19	16.00	15.14	16.78	3.27	15.76	9.51	22.01
Anthracene	2.19	2.05	2.63	2.29	4.04	3.04	3.24	3.44	3.60	3.11	2.72	3.14	0.64	2.96	1.74	4.18
Fluoranthene	9.05	7.78	10.62	9.15	16.46	12.35	13.87	14.23	16.59	14.53	12.65	14.59	3.08	12.66	6.77	18.54
Pyrene	3.12	2.77	3.89	3.26	5.48	3.81	4.32	4.54	4.71	4.14	3.54	4.13	0.82	3.98	2.41	5.54
Benz(a)anthracene	0.88	0.77	1.07	0.90	1.78	1.19	1.40	1.45	1.61	1.35	1.13	1.36	0.33	1.24	0.61	1.87
Chrysene	0.38	0.50	0.91	0.60	0.71	0.42	0.69	0.61	1.31	1.13	0.93	1.12	0.32	0.78	0.16	1.39
Benzo(b+k)fluoranthene	0.64	0.53	0.76	0.64	0.95	0.99	1.21	1.05	1.34	1.15	0.96	1.15	0.27	0.95	0.44	1.46
Benzo(a)pyrene	0.22	0.20	0.24	0.22	0.39	0.31	0.39	0.36	0.30	0.27	0.27	0.28	0.07	0.29	0.15	0.42
Indeno(1,2,3-c,d)pyrene	0.07	0.06	0.09	0.07	0.15	0.10	0.12	0.12	0.15	0.12	0.10	0.12	0.03	0.11	0.04	0.17
Dibenz(a,h)anthracene	0.03	0.03	0.04	0.03	0.06	0.04	0.05	0.05	0.06	0.05	0.04	0.05	0.01	0.04	0.02	0.07
Benzo(g,h,i)perylene	0.07	0.06	0.09	0.07	0.15	0.10	0.12	0.12	0.14	0.12	0.10	0.12	0.03	0.10	0.05	0.16
Totals	42.18	39.06	50.15	43.80	69.83	53.33	57.45	60.20	66.70	57.08	52.10	58.63	10.09	54.21	34.94	73.48

Appendix B-1. Factorial Calculations for Low Level Contaminated Clay Soil

INTRODUCTORY COMMENTS FOR APPENDIX B-1 and B-2.

- The data contained in these appendices are the data for the factorial statistical calculations.

- The data is grouped by PAH compound, and the factorial analysis for one compound appears on one page.

- The data in the factorial calculations are the average values for the appropriate run. The units for these values are μg/g (μg PAHs per gram of dry soil).

- The data table for the factorial analysis of variance contains the significance of each factor studied.

- A plot of normal probability of the effects was made for total PAHs concentrations and acenaphthene for the clay soil. Reverse Yates Algorithm and the diagnostic check for normal distribution of the residuals was also done for these two data sets. These calculations and plots follow the factorial calculations for these PAH data sets. The normal plots and check of residuals are not included for the other PAH data sets.

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - TOTAL PAHs CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	90.89	86.95	75.00	252.8	521.46	1036.75	***2084.09***				
high	bottom	slow	81.20	93.68	93.74	268.6	515.29	1047.34	121.29	612.97	1	612.97	10.108
low	top	slow	75.27	76.87	79.54	231.7	522.82	67.71	-4.47	0.83	1	0.83	-0.373
high	top	slow	83.23	90.81	109.57	283.6	524.52	53.58	67.65	190.69	1	190.69	5.637
low	bottom	fast	85.28	83.41	87.20	255.9	15.78	-6.17	10.59	4.67	1	4.67	0.882
high	bottom	fast	83.65	96.84	86.44	266.9	51.93	1.70	-14.13	8.32	1	8.32	-1.178
low	top	fast	76.57	81.17	83.25	241.0	11.04	36.15	7.87	2.58	1	2.58	0.656
high	top	fast	82.44	100.90	100.19	283.5	42.54	31.50	-4.65	0.90	1	0.90	-0.388
				Total sum of data=		*2084.1*			**Sum=**	**820.96**			
				Sum of squares of data=		182761.54			**Error=**	**964.28**	16	60.27	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**1785.25**			
			545392	**1090784**	**2181567**	**4363134**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	612.97	1	612.97	10.17	yes-99%
b=location	0.83	1	0.83	0.01	no
ab	190.69	1	190.69	3.16	no
c=fr.rate	4.67	1	4.67	0.08	no
ac	8.32	1	8.32	0.14	no
ac	2.58	1	2.58	0.04	no
abc	0.90	1	0.90	0.01	no
Error	964.28	16	60.27		

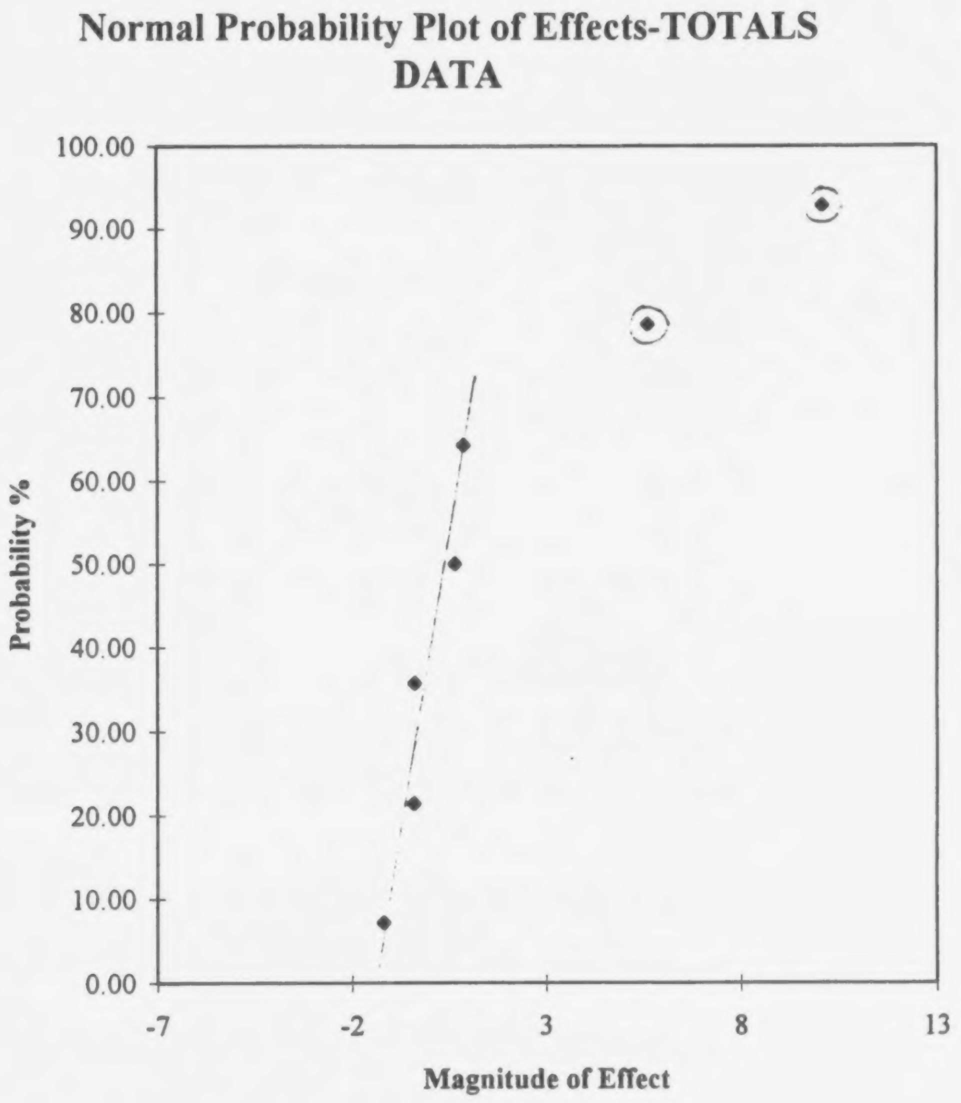
f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - LOG TRANSFORMED TOTAL PAHs CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	1.96	1.94	1.88	5.8	11.63	23.21	***46.48***				
high	bottom	slow	1.91	1.97	1.97	5.9	11.58	23.27	0.60	0.01	1	0.01	0.050
low	top	slow	1.88	1.89	1.90	5.7	11.64	0.34	-0.05	0.00	1	0.00	-0.004
high	top	slow	1.92	1.96	2.04	5.9	11.63	0.26	0.33	0.00	1	0.00	0.027
low	bottom	fast	1.93	1.92	1.94	5.8	0.08	-0.04	0.07	0.00	1	0.00	0.005
high	bottom	fast	1.92	1.99	1.94	5.8	0.26	0.00	-0.08	0.00	1	0.00	-0.006
low	top	fast	1.88	1.91	1.92	5.7	0.05	0.17	0.04	0.00	1	0.00	0.003
high	top	fast	1.92	2.00	2.00	5.9	0.21	0.15	-0.02	0.00	1	0.00	-0.002
					Total sum of data=	***46.5***			**Sum=**	**0.02**			
					Sum of squares of data=	90.06			**Error=**	**0.02**	16	0.00	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**0.04**			
			270	**540**	**1080**	**2161**							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.01	1	0.01	10.63	yes-99%
b=location	0.00	1	0.00	0.07	no
ab	0.00	1	0.00	3.25	no
c=fr.rate	0.00	1	0.00	0.13	no
ac	0.00	1	0.00	0.17	no
ac	0.00	1	0.00	0.05	no
abc	0.00	1	0.00	0.01	no
Error	0.02	16	0.00		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53


Normal Probability Plot of Effects-TOTALS DATA
Probability %
100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
-7
-2
3
8
13
Magnitude of Effect

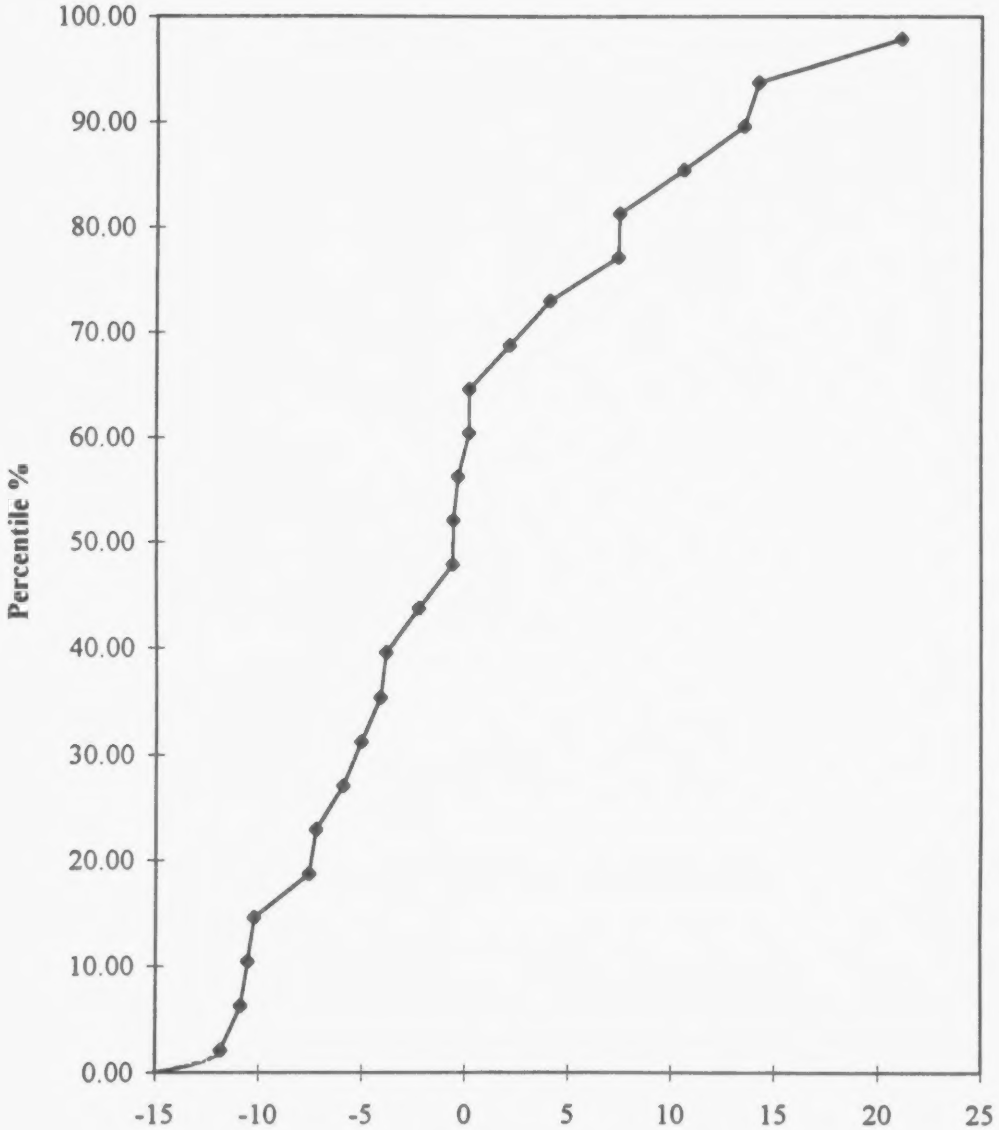
DIAGNOSTIC CHECK- REVERSE YATES ALGORITHM

						Predicted y				Residuals=actual-predicted		
	Effects	(1)	(2)	(3)	Divisor	y^	Actual y values			y-y^		
abc	0.00	0.00	0.00	*2099.52*	24	87.48	90.89	86.95	75.00	3.41	-0.53	-12.48
bc	0.00	0.00	2094.23	2068.64	24	86.19	81.20	93.68	93.74	-5.00	7.48	7.54
ac	0.00	5.29	0.00	2088.93	24	87.04	75.27	76.87	79.54	-11.77	-10.17	-7.50
c=rate	0.00	2094.23	2068.64	2079.23	24	86.63	83.23	90.81	109.57	-3.40	4.18	22.94
ab	5.29	0.00	0.00	2099.52	24	87.48	85.30	83.41	87.20	-2.18	-4.07	-0.28
b	0.00	0.00	2088.93	2068.64	24	86.19	83.65	96.84	86.44	-2.54	10.64	0.25
a=freezing	10.14	-5.29	0.00	2088.93	24	87.04	76.57	81.17	83.25	-10.47	-5.87	-3.79
avg	2084.08	2073.94	2079.23	2079.23	24	86.63	82.44	100.90	100.19	-4.19	14.27	13.56
	2099.52											

Sums of squares check:

4343531	8687062	17351921	34748246
Effects	(1)	(2)	(3)

Normal Probability Plot for Residuals for TOTALS data



FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - ACENAPHTHENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	26.83	22.58	21.78	71.2	150.04	298.80	*585.03*				
high	bottom	slow	24.91	28.52	25.42	78.9	148.76	286.23	39.71	65.70	1	65.70	3.309
low	top	slow	24.79	20.91	21.29	67.0	141.05	22.44	2.85	0.34	1	0.34	0.238
high	top	slow	25.63	27.72	28.42	81.8	145.18	17.27	11.61	5.62	1	5.62	0.967
low	bottom	fast	22.44	23.26	21.63	67.3	7.66	-1.28	-12.57	6.58	1	6.58	-1.048
high	bottom	fast	23.26	26.25	24.21	73.7	14.78	4.13	-5.17	1.11	1	1.11	-0.431
low	top	fast	21.28	23.87	22.00	67.2	6.39	7.12	5.41	1.22	1	1.22	0.451
high	top	fast	23.95	26.97	27.11	78.0	10.88	4.49	-2.63	0.29	1	0.29	-0.219
					Total sum of data=	*585.0*			**Sum=**	**80.86**			
					Sum of squares of data=	14393.38			**Error=**	**51.68**	16	3.23	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**132.54**			
			43025	**86050**	**172100**	**344201**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	65.70	1	65.70	20.34	yes-99%
b=location	0.34	1	0.34	0.10	no
ab	5.62	1	5.62	1.74	no
c=fr.rate	6.58	1	6.58	2.04	no
ac	1.11	1	1.11	0.34	no
ac	1.22	1	1.22	0.38	no
abc	0.29	1	0.29	0.09	no
Error	51.68	16	3.23		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - LOG TRANSFORMED ACENAPHTHENE CONCENTRATION DATA

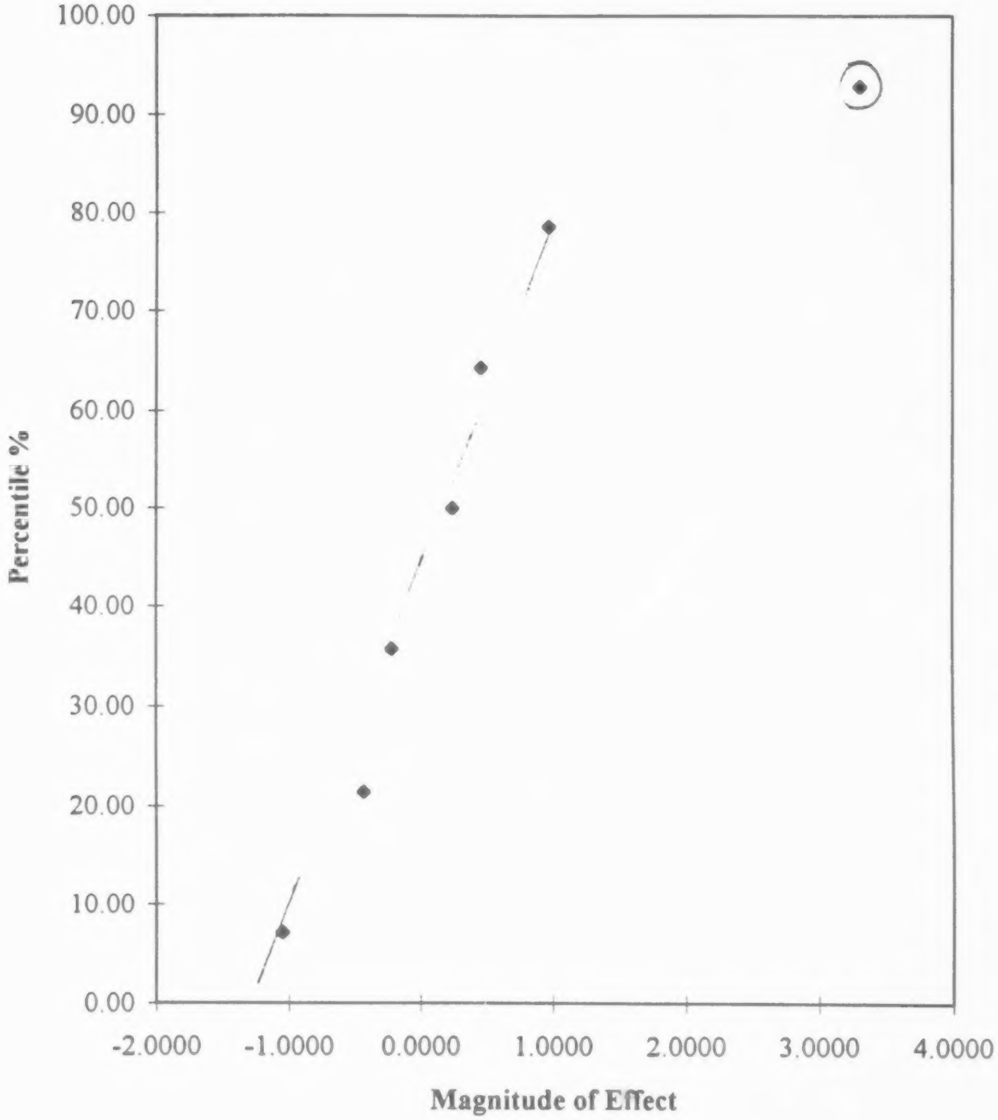
VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	1.43	1.35	1.34	4.1	8.38	16.73	*33.24*				
high	bottom	slow	1.40	1.46	1.41	4.3	8.35	16.51	0.71	0.02	1	0.02	0.059
low	top	slow	1.39	1.32	1.33	4.0	8.22	0.40	0.04	0.00	1	0.00	0.003
high	top	slow	1.41	1.44	1.45	4.3	8.29	0.31	0.20	0.00	1	0.00	0.017
low	bottom	fast	1.35	1.37	1.34	4.1	0.14	-0.03	-0.21	0.00	1	0.00	-0.018
high	bottom	fast	1.37	1.42	1.38	4.2	0.26	0.07	-0.09	0.00	1	0.00	-0.007
low	top	fast	1.33	1.38	1.34	4.0	0.12	0.13	0.10	0.00	1	0.00	0.008
high	top	fast	1.38	1.43	1.43	4.2	0.20	0.08	-0.05	0.00	1	0.00	-0.004
					Total sum of data=	*33.2*			**Sum=**	**0.03**			
					Sum of squares of data=	46.08			**Error=**	**0.02**	16	0.00	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**0.04**			
			138	**276**	**553**	**1105**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.02	1	0.02	20.80	yes-99%
b=location	0.00	1	0.00	0.07	no
ab	0.00	1	0.00	1.71	no
c=fr.rate	0.00	1	0.00	1.83	no
ac	0.00	1	0.00	0.31	no
ac	0.00	1	0.00	0.40	no
abc	0.00	1	0.00	0.10	no
Error	0.02	16	0.00		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

Normal Probability Plot for Acenaphthene

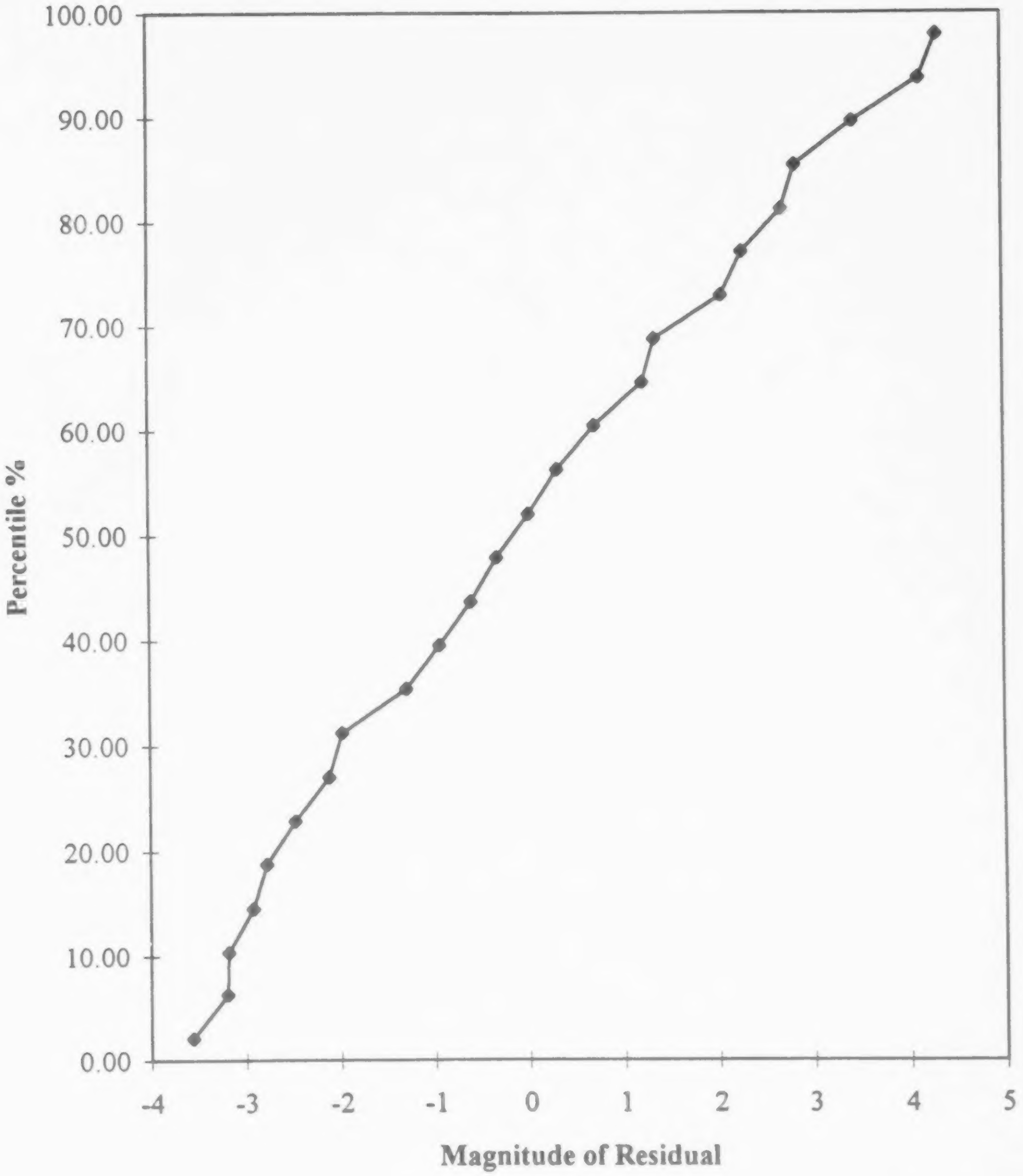


DIAGNOSTIC CHECK- REVERSE YATES ALGORITHM

						Predicted y				Residuals=actual-predicted		
	Effects	(1)	(2)	(3)	Divisor	y^		Actual y values			y-y^	
abc	0.00	0.00	0.00	***589.31***	24	24.55	26.83	22.58	21.78	2.28	-1.97	-2.77
bc	0.00	0.00	588.34	580.75	24	24.20	24.91	28.52	25.42	0.71	4.32	1.22
ac	0.00	0.97	0.00	587.37	24	24.47	24.79	20.91	21.29	0.32	-3.56	-3.18
c=rate	0.00	588.34	580.75	582.69	24	24.28	25.63	27.72	28.42	1.35	3.44	4.14
ab	0.97	0.00	0.00	589.31	24	24.55	22.44	23.26	21.63	-2.11	-1.29	-2.92
b	0.00	0.00	587.37	580.75	24	24.20	23.26	26.25	24.21	-0.94	2.05	0.01
a=freezing	3.31	-0.97	0.00	587.37	24	24.47	21.28	23.87	22.00	-3.19	-0.60	-2.47
avg	585.03	581.72	582.69	582.69	24	24.28	23.95	26.97	27.11	-0.33	2.69	2.83
	589.31											

Sums of squares check:

342272	684544	1367949	2738176
Effects	(1)	(2)	(3)



Normal Probability Plot of Residuals for ACENAPHTHENE

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - FLUORENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	21.44	19.89	18.36	59.7	123.90	245.94	*492.37*				
high	bottom	slow	20.29	22.08	21.84	64.2	122.04	246.43	30.75	39.40	1	39.40	2.563
low	top	slow	18.65	17.82	17.67	54.1	122.87	18.28	-1.17	0.06	1	0.06	-0.098
high	top	slow	21.23	21.89	24.78	67.9	123.56	12.47	15.81	10.41	1	10.41	1.318
low	bottom	fast	19.99	20.04	19.93	60.0	4.52	-1.86	0.49	0.01	1	0.01	0.041
high	bottom	fast	19.37	23.12	20.42	62.9	13.76	0.69	-5.81	1.41	1	1.41	-0.484
low	top	fast	18.16	19.13	19.73	57.0	2.95	9.24	2.55	0.27	1	0.27	0.212
high	top	fast	19.24	23.89	23.41	66.5	9.52	6.57	-2.67	0.30	1	0.30	-0.223
					Total sum of data=	*492.4*			Sum=	51.85			
					Sum of squares of data=	10189.18			Error=	36.15	16	2.26	
			Check:	**(1)**	**(2)**	**(3)**			S.S.total=	**88.00**			
			30459	**60918**	**121836**	**243673**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	39.40	1	39.40	17.44	yes-99%
b=location	0.06	1	0.06	0.03	no
ab	10.41	1	10.41	4.61	yes-95%
c=fr.rate	0.01	1	0.01	0.00	no
ac	1.41	1	1.41	0.62	no
ac	0.27	1	0.27	0.12	no
abc	0.30	1	0.30	0.13	no
Error	36.15	16	2.26		

f 0.05 (1,16)=4.49

f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - LOG TRANSFORMED FLUORENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	1.3312	1.2986	1.2639	3.9	7.88	15.71	*31.45*				
high	bottom	slow	1.3073	1.3440	1.3393	4.0	7.83	15.73	0.64	0.02	1	0.02	0.054
low	top	slow	1.2707	1.2509	1.2472	3.8	7.86	0.39	-0.05	0.00	1	0.00	-0.004
high	top	slow	1.3269	1.3402	1.3941	4.1	7.87	0.25	0.33	0.00	1	0.00	0.028
low	bottom	fast	1.3008	1.3019	1.2995	3.9	0.10	-0.05	0.02	0.00	1	0.00	0.001
high	bottom	fast	1.2871	1.3640	1.3101	4.0	0.29	0.00	-0.13	0.00	1	0.00	-0.011
low	top	fast	1.2591	1.2817	1.2951	3.8	0.06	0.20	0.06	0.00	1	0.00	0.005
high	top	fast	1.2842	1.3782	1.3694	4.0	0.20	0.14	-0.06	0.00	1	0.00	-0.005
					Total sum of data=	*31.4*			**Sum=**	**0.02**			
					Sum of squares of data=	41.24			**Error=**	**0.02**	16	0.00	
			Check:	(1)	(2)	(3)			**S.S.total=**	**0.04**			
			124	**247**	**495**	**989**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.02	1	0.02	18.34	yes-95%
b=location	0.00	1	0.00	0.11	no
ab	0.00	1	0.00	4.89	yes-95%
c=fr.rate	0.00	1	0.00	0.01	no
ac	0.00	1	0.00	0.80	no
ac	0.00	1	0.00	0.15	no
abc	0.00	1	0.00	0.15	no
Error	0.02	16	0.00		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - PHANANTHRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	22.69	26.61	21.20	70.5	148.33	296.17	***616.26***				
high	bottom	slow	22.37	25.62	29.84	77.8	147.84	320.09	46.88	91.57	1	91.57	3.907
low	top	slow	19.41	23.56	21.79	64.8	159.96	25.65	-0.32	0.00	1	0.00	-0.027
high	top	slow	22.89	25.06	35.13	83.1	160.13	21.23	23.94	23.88	1	23.88	1.995
low	bottom	fast	25.97	23.80	28.14	77.9	7.33	-0.49	23.92	23.84	1	23.84	1.993
high	bottom	fast	26.54	29.64	25.87	82.1	18.32	0.17	-4.42	0.81	1	0.81	-0.368
low	top	fast	22.87	22.38	26.27	71.5	4.14	10.99	0.66	0.02	1	0.02	0.055
high	top	fast	25.98	32.18	30.45	88.6	17.09	12.95	1.96	0.16	1	0.16	0.163
					Total sum of data=	***616.3***			**Sum=**	**140.29**			
					Sum of squares of data=	16148.92			**Error=**	**184.62**	16	11.54	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**324.91**			
			47893	**95786**	**191572**	**383143**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	91.57	1	91.57	7.94	yes-95%
b=location	0.00	1	0.00	0.00	no
ab	23.88	1	23.88	2.07	no
c=fr.rate	23.84	1	23.84	2.07	no
ac	0.81	1	0.81	0.07	no
ac	0.02	1	0.02	0.00	no
abc	0.16	1	0.16	0.01	no
Error	184.62	16	11.54		

f0.05 (1,16)=4.49

f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - FLUORANTHENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	13.57	11.62	9.01	34.2	66.63	135.04	*261.28*				
high	bottom	slow	9.33	11.40	11.70	32.4	68.41	126.24	9.00	3.38	1	3.38	0.750
low	top	slow	12.84	10.16	9.99	33.0	63.28	0.66	1.46	0.09	1	0.09	0.122
high	top	slow	9.56	10.74	15.12	35.4	62.96	8.34	7.30	2.22	1	2.22	0.608
low	bottom	fast	10.11	9.30	10.92	30.3	-1.77	1.78	-8.80	3.23	1	3.23	-0.733
high	bottom	fast	10.30	11.84	10.81	33.0	2.43	-0.32	7.68	2.46	1	2.46	0.640
low	top	fast	9.11	10.01	9.50	28.6	2.62	4.20	-2.10	0.18	1	0.18	-0.175
high	top	fast	9.70	11.45	13.19	34.3	5.72	3.10	-1.10	0.05	1	0.05	-0.092
					Total sum of data=	***261.3***			**Sum=**	**11.60**			
					Sum of squares of data=	2901.19			**Error=**	**45.12**	16	2.82	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**56.72**			
			8568	**17136**	**34273**	**68546**							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	3.38	1	3.38	1.20	no
b=location	0.09	1	0.09	0.03	no
ab	2.22	1	2.22	0.79	no
c=fr.rate	3.23	1	3.23	1.14	no
ac	2.46	1	2.46	0.87	no
ac	0.18	1	0.18	0.07	no
abc	0.05	1	0.05	0.02	no
Error	45.12	16	2.82		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - PYRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	2.64	2.51	2.22	7.4	17.00	33.88	*71.69*				
high	bottom	slow	2.35	4.08	3.20	9.6	16.88	37.81	9.93	4.11	1	4.11	0.828
low	top	slow	2.41	2.22	2.20	6.8	19.29	5.48	-0.89	0.03	1	0.03	-0.074
high	top	slow	2.32	3.62	4.11	10.1	18.52	4.45	2.51	0.26	1	0.26	0.209
low	bottom	fast	2.97	2.77	3.18	8.9	2.26	-0.12	3.93	0.64	1	0.64	0.328
high	bottom	fast	2.74	3.98	3.65	10.4	3.22	-0.77	-1.03	0.04	1	0.04	-0.086
low	top	fast	2.52	2.60	2.64	7.8	1.45	0.96	-0.65	0.02	1	0.02	-0.054
high	top	fast	2.59	3.82	4.35	10.8	3.00	1.55	0.59	0.01	1	0.01	0.049
					Total sum of data=	71.7			Sum=	5.12			
					Sum of squares of data=	225.14			Error=	5.87	16	0.37	
			Check:	(1)	(2)	(3)			S.S.total=	11.00			
			658	1316	2631	5262							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	4.11	1	4.11	11.19	yes-99%
b=location	0.03	1	0.03	0.09	no
ab	0.26	1	0.26	0.72	no
c=fr.rate	0.64	1	0.64	1.75	no
ac	0.04	1	0.04	0.12	no
ac	0.02	1	0.02	0.05	no
abc	0.01	1	0.01	0.04	no
Error	5.87	16	0.37		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR CLAY - LOG TRANSFORMED PYRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	0.42	0.40	0.35	1.2	2.65	5.26	***11.15***				
high	bottom	slow	0.37	0.61	0.51	1.5	2.61	5.89	1.36	0.08	1	0.08	0.114
low	top	slow	0.38	0.35	0.34	1.1	3.02	0.79	-0.19	0.00	1	0.00	-0.016
high	top	slow	0.37	0.56	0.61	1.5	2.87	0.58	0.36	0.01	1	0.01	0.030
low	bottom	fast	0.47	0.44	0.50	1.4	0.32	-0.05	0.63	0.02	1	0.02	0.052
high	bottom	fast	0.44	0.60	0.56	1.6	0.47	-0.15	-0.21	0.00	1	0.00	-0.017
low	top	fast	0.40	0.41	0.42	1.2	0.18	0.15	-0.10	0.00	1	0.00	-0.008
high	top	fast	0.41	0.58	0.64	1.6	0.40	0.21	0.07	0.00	1	0.00	0.005
					Total sum of data=	*11.2*			**Sum=**	**0.10**			
					Sum of squares of data=	5.40			**Error=**	**0.11**	16	0.01	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**0.21**			
			16	**32**	**63**	**127**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.08	1	0.08	11.22	yes-99%
b=location	0.00	1	0.00	0.22	no
ab	0.01	1	0.01	0.79	no
c=fr.rate	0.02	1	0.02	2.36	no
ac	0.00	1	0.00	0.26	no
ac	0.00	1	0.00	0.06	no
abc	0.00	1	0.00	0.03	no
Error	0.11	16	0.01		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

Appendix B-2. Factorial Calculations for Highly Contaminated Sand Soil

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - TOTAL PAHs CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	40.33	49.37	57.57	147.3	283.81	568.35	*1223.42*				
high	bottom	slow	33.26	50.62	52.66	136.5	284.54	655.07	26.30	28.82	1	28.82	2.192
low	top	slow	49.78	47.33	48.10	145.2	312.68	-16.61	30.44	38.61	1	38.61	2.537
high	top	slow	38.98	51.66	48.69	139.3	342.39	42.91	22.60	21.28	1	21.28	1.883
low	bottom	fast	49.23	41.47	59.35	150.1	-10.73	0.73	86.72	313.35	1	313.35	7.227
high	bottom	fast	43.80	60.20	58.63	162.6	-5.88	29.71	59.52	147.61	1	147.61	4.960
low	top	fast	40.07	53.47	62.49	156.0	12.58	4.85	28.98	34.99	1	34.99	2.415
high	top	fast	68.55	63.79	54.02	186.4	30.33	17.75	12.90	6.93	1	6.93	1.075
				Total sum of data=		*1223.4*			Sum=	591.60			
				Sum of squares of data=		64112.40			Error=	1155.95	16	72.25	
			Check:	(1)	(2)	(3)			S.S.total=	1747.55			
			188869	377739	755477	1510955							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	28.82	1	28.82	0.40	no
b=location	38.61	1	38.61	0.53	no
ab	21.28	1	21.28	0.29	no
c=fr.rate	313.35	1	313.35	4.34	no
ac	147.61	1	147.61	2.04	no
ac	34.99	1	34.99	0.48	no
abc	6.93	1	6.93	0.10	no
Error	1155.95	16	72.25		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - NAPHTHALENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	7.30	5.60	4.10	17.00	25.12	51.23	*84.27*				
high	bottom	slow	3.59	1.53	3.00	8.12	26.11	33.04	-45.03	84.49	1	84.49	-3.753
low	top	slow	7.40	5.87	4.83	18.10	15.74	-18.97	2.55	0.27	1	0.27	0.213
high	top	slow	3.86	1.36	2.79	8.01	17.30	-26.06	-2.43	0.25	1	0.25	-0.203
low	bottom	fast	7.43	5.17	1.48	14.08	-8.88	0.99	-18.19	13.79	1	13.79	-1.516
high	bottom	fast	0.46	0.64	0.56	1.66	-10.09	1.56	-7.09	2.09	1	2.09	-0.591
low	top	fast	7.87	5.70	1.90	15.47	-12.42	-1.21	0.57	0.01	1	0.01	0.048
high	top	fast	0.49	0.64	0.70	1.83	-13.64	-1.22	-0.01	0.00	1	0.00	-0.001
					Total sum of data=	*84.3*			Sum=	100.90			
					Sum of squares of data=	447.00			Error=	50.21	16	3.14	
			Check:	(1)	(2)	(3)			S.S.total=	151.11			
			1190	2381	4762	9523							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	84.49	1	84.49	26.92	yes-99%
b=location	0.27	1	0.27	0.09	no
ab	0.25	1	0.25	0.08	no
c=fr.rate	13.79	1	13.79	4.39	no
ac	2.09	1	2.09	0.67	no
ac	0.01	1	0.01	0.00	no
abc	0.00	1	0.00	0.00	no
Error	50.21	16	3.14		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - LOG TRANSFORMED NAPHTHALENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	0.86	0.75	0.61	2.22	3.44	6.93	9.17				
high	bottom	slow	0.56	0.18	0.48	1.22	3.49	2.24	-7.29	2.21	1	2.21	-0.608
low	top	slow	0.87	0.77	0.68	2.32	0.97	-2.16	0.35	0.01	1	0.01	0.029
high	top	slow	0.59	0.13	0.45	1.17	1.27	-5.13	-0.20	0.00	1	0.00	-0.017
low	bottom	fast	0.87	0.71	0.17	1.75	-1.01	0.05	-4.68	0.91	1	0.91	-0.390
high	bottom	fast	-0.34	-0.19	-0.25	-0.78	-1.16	0.30	-2.96	0.37	1	0.37	-0.247
low	top	fast	0.90	0.76	0.28	1.93	-2.54	-0.15	0.25	0.00	1	0.00	0.021
high	top	fast	-0.31	-0.19	-0.15	-0.66	-2.59	-0.05	0.10	0.00	1	0.00	0.008
					Total sum of data=	9.2			Sum=	3.50			
					Sum of squares of data=	7.75			Error=	0.74	16	0.05	
			Check:	(1)	(2)	(3)			S.S.total=	4.24			
			21	42	84	168							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	2.21	1	2.21	48.17	yes-99%
b=location	0.01	1	0.01	0.11	no
ab	0.00	1	0.00	0.04	no
c=fr.rate	0.91	1	0.91	19.89	yes-99%
ac	0.37	1	0.37	7.96	yes-95%
ac	0.00	1	0.00	0.06	no
abc	0.00	1	0.00	0.01	no
Error	0.74	16	0.05		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - ACENAPHTHENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	6.37	6.67	9.07	22.1	45.29	90.40	***189.83***				
high	bottom	slow	5.99	8.75	8.44	23.2	45.11	99.43	5.17	1.11	1	1.11	0.431
low	top	slow	7.07	7.00	7.67	21.7	47.86	2.70	3.53	0.52	1	0.52	0.294
high	top	slow	6.83	8.30	8.24	23.4	51.57	2.47	2.31	0.22	1	0.22	0.193
low	bottom	fast	7.23	6.87	9.65	23.8	1.07	-0.18	9.03	3.40	1	3.40	0.753
high	bottom	fast	7.71	8.15	8.25	24.1	1.63	3.71	-0.23	0.00	1	0.00	-0.019
low	top	fast	6.83	8.03	9.87	24.7	0.36	0.56	3.89	0.63	1	0.63	0.324
high	top	fast	10.00	8.38	8.46	26.8	2.11	1.75	1.19	0.06	1	0.06	0.099
					Total sum of data=	***189.8***			**Sum=**	**5.94**			
					Sum of squares of data=	1529.12			**Error=**	**21.70**	16	1.36	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**27.65**			
			4522	**9045**	**18089**	**36178**							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	1.11	1	1.11	0.82	no
b=location	0.52	1	0.52	0.38	no
ab	0.22	1	0.22	0.16	no
c=fr.rate	3.40	1	3.40	2.51	no
ac	0.00	1	0.00	0.00	no
ac	0.63	1	0.63	0.46	no
abc	0.06	1	0.06	0.04	no
Error	21.70	16	1.36		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - FLUORENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	5.47	6.07	7.77	19.3	38.00	75.35	*156.41*				
high	bottom	slow	4.84	6.89	6.96	18.7	37.35	81.06	2.49	0.26	1	0.26	0.208
low	top	slow	6.40	5.87	6.13	18.4	39.04	-0.07	2.33	0.23	1	0.23	0.194
high	top	slow	5.60	6.67	6.68	19.0	42.02	2.56	3.37	0.47	1	0.47	0.281
low	bottom	fast	6.43	5.43	7.57	19.4	-0.62	-0.65	5.71	1.36	1	1.36	0.476
high	bottom	fast	5.80	7.07	6.74	19.6	0.55	2.98	2.63	0.29	1	0.29	0.219
low	top	fast	5.37	6.50	7.95	19.8	0.18	1.17	3.63	0.55	1	0.55	0.303
high	top	fast	8.12	7.32	6.76	22.2	2.38	2.20	1.03	0.04	1	0.04	0.086
					Total sum of data=	*156.4*			Sum=	3.20			
					Sum of squares of data=	1036.63			Error=	14.10	16	0.88	
			Check:	(1)	(2)	(3)			S.S.total=	17.30			
			3068	6135	12270	24541							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.26	1	0.26	0.29	no
b=location	0.23	1	0.23	0.26	no
ab	0.47	1	0.47	0.54	no
c=fr.rate	1.36	1	1.36	1.54	no
ac	0.29	1	0.29	0.33	no
ac	0.55	1	0.55	0.62	no
abc	0.04	1	0.04	0.05	no
Error	14.10	16	0.88		

f0.05 (1,16)=4.49

f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - PHENANTHRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	11.37	13.90	15.25	40.52	78.03	157.43	*342.20*				
high	bottom	slow	9.02	14.19	14.30	37.51	79.40	184.77	13.46	7.55	1	7.55	1.122
low	top	slow	14.30	13.10	12.93	40.33	88.23	-4.27	9.68	3.90	1	3.90	0.807
high	top	slow	10.63	14.29	14.15	39.07	96.54	17.73	6.82	1.94	1	1.94	0.568
low	bottom	fast	14.17	11.60	15.18	40.95	-3.01	1.37	27.34	31.14	1	31.14	2.278
high	bottom	fast	12.39	18.11	16.78	47.28	-1.26	8.31	22.00	20.17	1	20.17	1.833
low	top	fast	11.23	15.30	16.04	42.57	6.33	1.75	6.94	2.01	1	2.01	0.578
high	top	fast	18.86	19.12	15.99	53.97	11.40	5.07	3.32	0.46	1	0.46	0.277
					Total sum of data=	*342.2*			**Sum=**	**67.17**			
					Sum of squares of data=	5026.24			**Error=**	**79.87**	16	4.99	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**147.04**			
			14839	**29678**	**59356**	**118713**							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	7.55	1	7.55	1.51	no
b=location	3.90	1	3.90	0.78	no
ab	1.94	1	1.94	0.39	no
c=fr.rate	31.14	1	31.14	6.24	yes-95%
ac	20.17	1	20.17	4.04	no
ac	2.01	1	2.01	0.40	no
abc	0.46	1	0.46	0.09	no
Error	79.87	16	4.99		

f0.05 (1,16)=4.49

f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - LOG TRANSFORMED PHENANTHRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	1.06	1.14	1.18	3.38	6.64	13.36	*27.54*				
high	bottom	slow	0.96	1.15	1.16	3.26	6.72	14.17	0.33	0.00	1	0.00	0.027
low	top	slow	1.16	1.12	1.11	3.38	6.97	-0.17	0.30	0.00	1	0.00	0.025
high	top	slow	1.03	1.16	1.15	3.33	7.20	0.50	0.21	0.00	1	0.00	0.017
low	bottom	fast	1.15	1.06	1.18	3.40	-0.12	0.07	0.81	0.03	1	0.03	0.068
high	bottom	fast	1.09	1.26	1.22	3.58	-0.05	0.23	0.67	0.02	1	0.02	0.056
low	top	fast	1.05	1.18	1.21	3.44	0.18	0.07	0.16	0.00	1	0.00	0.013
high	top	fast	1.28	1.28	1.20	3.76	0.32	0.14	0.07	0.00	1	0.00	0.006
				Total sum of data=		*27.5*			Sum=	0.06			
				Sum of squares of data=		31.74			Error=	0.09	16	0.01	
			Check:	(1)	(2)	(3)			S.S.total=	0.14			
			95	190	380	760							

Data Table for Analysis of Variance					
Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.00	1	0.00	0.82	no
b=location	0.00	1	0.00	0.69	no
ab	0.00	1	0.00	0.34	no
c=fr.rate	0.03	1	0.03	5.06	yes-95%
ac	0.02	1	0.02	3.45	no
ac	0.00	1	0.00	0.19	no
abc	0.00	1	0.00	0.04	no
Error	0.09	16	0.01		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - PHENANTHRENE CONCENTRATION DATA

CORRECTED

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	11.37	13.90	15.25	40.52	83.26	162.66	*341.43*				
high	bottom	slow	14.25	14.19	14.30	42.74	79.40	178.77	12.69	6.70	1	6.70	1.057
low	top	slow	14.30	13.10	12.93	40.33	88.23	0.96	-1.55	0.10	1	0.10	-0.129
high	top	slow	10.63	14.29	14.15	39.07	90.54	11.73	-4.41	0.81	1	0.81	-0.367
low	bottom	fast	14.17	11.60	15.18	40.95	2.22	-3.85	16.12	10.82	1	10.82	1.343
high	bottom	fast	12.39	18.11	16.78	47.28	-1.26	2.31	10.78	4.84	1	4.84	0.898
low	top	fast	11.23	15.30	16.04	42.57	6.33	-3.48	6.16	1.58	1	1.58	0.514
high	top	fast	15.99	15.99	15.99	47.97	5.40	-0.93	2.55	0.27	1	0.27	0.212
					Total sum of data=	*341.4*			Sum=	25.12			
					Sum of squares of data=	4937.88			Error=	55.63	16	3.48	
			Check:	**(1)**	**(2)**	**(3)**			S.S.total=	**80.76**			
			14647	**29294**	**58587**	**117174**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	6.70	1	6.70	1.93	no
b=location	0.10	1	0.10	0.03	no
ab	0.81	1	0.81	0.23	no
c=fr.rate	10.82	1	10.82	3.11	no
ac	4.84	1	4.84	1.39	no
ac	1.58	1	1.58	0.46	no
abc	0.27	1	0.27	0.08	no
Error	55.63	16	3.48		

f0.05 (1,16)=4.49
f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - FLUORANTHENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	5.40	8.47	14.10	28.0	58.22	112.63	*253.19*				
high	bottom	slow	5.78	12.00	12.47	30.3	54.41	140.56	39.47	64.91	1	64.91	3.289
low	top	slow	7.77	7.67	8.43	23.9	65.05	8.95	6.65	1.84	1	1.84	0.554
high	top	slow	7.07	13.29	10.18	30.5	75.51	30.52	13.13	7.18	1	7.18	1.094
low	bottom	fast	7.40	6.77	12.91	27.1	2.28	-3.81	27.93	32.50	1	32.50	2.328
high	bottom	fast	9.15	14.23	14.59	38.0	6.67	10.46	21.57	19.39	1	19.39	1.798
low	top	fast	4.60	9.80	13.54	27.9	10.89	4.39	14.27	8.48	1	8.48	1.189
high	top	fast	20.13	15.04	12.40	47.6	19.63	8.74	4.35	0.79	1	0.79	0.363

Total sum of data= *253.2*

Sum of squares of data= 3005.18

Check:	(1)	(2)	(3)
8418	16837	33674	67348

Sum= **135.10**

Error= **199.03** 16 12.44

S.S.total= **334.13**

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	64.91	1	64.91	5.22	yes-95%
b=location	1.84	1	1.84	0.15	no
ab	7.18	1	7.18	0.58	no
c=fr.rate	32.50	1	32.50	2.61	no
ac	19.39	1	19.39	1.56	no
ac	8.48	1	8.48	0.68	no
abc	0.79	1	0.79	0.06	no
Error	199.03	16	12.44		no

f 0.05 (1,16)=4.49

f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - LOG TRANSFORMED FLUORANTHENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	0.73	0.93	1.15	2.81	5.75	11.43	*23.88*				
high	bottom	slow	0.76	1.08	1.10	2.94	5.68	12.45	1.66	0.12	1	0.12	0.139
low	top	slow	0.89	0.88	0.93	2.70	6.09	0.41	0.21	0.00	1	0.00	0.017
high	top	slow	0.85	1.12	1.01	2.98	6.36	1.26	0.47	0.01	1	0.01	0.039
low	bottom	fast	0.87	0.83	1.11	2.81	0.13	-0.06	1.02	0.04	1	0.04	0.085
high	bottom	fast	0.96	1.15	1.16	3.28	0.28	0.27	0.85	0.03	1	0.03	0.071
low	top	fast	0.66	0.99	1.13	2.79	0.47	0.15	0.34	0.00	1	0.00	0.028
high	top	fast	1.30	1.18	1.09	3.57	0.79	0.32	0.17	0.00	1	0.00	0.014
				Total sum of data=		*23.9*			Sum=	**0.21**			
				Sum of squares of data=		24.37			**Error=**	**0.41**	16	0.03	
			Check:	**(1)**	**(2)**	**(3)**			**S.S.total=**	**0.61**			
			72	**144**	**288**	**575**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.12	1	0.12	4.53	yes-95%
b=location	0.00	1	0.00	0.07	no
ab	0.01	1	0.01	0.37	no
c=fr.rate	0.04	1	0.04	1.71	no
ac	0.03	1	0.03	1.18	no
ac	0.00	1	0.00	0.18	no
abc	0.00	1	0.00	0.05	no
Error	0.41	16	0.03		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - PYRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	1.77	3.33	5.20	10.30	18.05	34.81	***80.44***				
high	bottom	slow	1.86	2.83	3.06	7.75	16.76	45.63	0.74	0.02	1	0.02	0.062
low	top	slow	2.67	3.07	3.00	8.74	22.24	-3.27	-0.14	0.00	1	0.00	-0.012
high	top	slow	2.23	3.19	2.60	8.02	23.39	4.01	2.60	0.28	1	0.28	0.217
low	bottom	fast	2.43	2.27	5.61	10.31	-2.55	-1.29	10.82	4.88	1	4.88	0.902
high	bottom	fast	3.26	4.54	4.13	11.93	-0.72	1.15	7.28	2.21	1	2.21	0.607
low	top	fast	1.57	3.23	5.70	10.50	1.62	1.83	2.44	0.25	1	0.25	0.203
high	top	fast	4.64	4.81	3.44	12.89	2.39	0.77	-1.06	0.05	1	0.05	-0.088
					Total sum of data=	***80.4***			**Sum=**	7.69			
					Sum of squares of data=	302.27			**Error=**	**24.98**	16	1.56	
			Check:	(1)	(2)	(3)			**S.S.total=**	**32.66**			
			832	**1664**	**3328**	**6655**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.02	1	0.02	0.01	no
b=location	0.00	1	0.00	0.00	no
ab	0.28	1	0.28	0.18	no
c=fr.rate	4.88	1	4.88	3.13	no
ac	2.21	1	2.21	1.41	no
ac	0.25	1	0.25	0.16	no
abc	0.05	1	0.05	0.03	no
Error	24.98	16	1.56		

f0.05 (1,16)=4.49

f0.01 (1,16)=8.53

FACTORIAL TO ASSESS MOISTURE CONTENT, LOCATION OF CONTAMINATION, AND FREEZING RATE DATA FOR SAND - BENZO(b+k)PYRENE CONCENTRATION DATA

VARIABLE			CONCENTRATION DATA				YATES ALGORITHM TO CALCULATE EFFECTS						
Moisture	Location	Rate	Rep.1	Rep.2	Rep.3	TOTALS	(1)	(2)	(3)	SUM.SQ.	D.Fr.	Mean Sq.	Effects
low	bottom	slow	0.30	0.80	1.13	2.2	4.05	7.58	*17.79*				
high	bottom	slow	0.29	0.73	0.80	1.8	3.53	10.21	1.99	0.17	1	0.17	0.166
low	top	slow	0.57	0.60	0.67	1.8	4.76	-0.56	0.17	0.00	1	0.00	0.014
high	top	slow	0.38	0.69	0.62	1.7	5.45	2.55	0.97	0.04	1	0.04	0.081
low	bottom	fast	0.40	0.37	1.15	1.9	-0.41	-0.52	2.63	0.29	1	0.29	0.219
high	bottom	fast	0.64	1.05	1.15	2.8	-0.15	0.69	3.11	0.40	1	0.40	0.259
low	top	fast	0.20	0.50	1.21	1.9	0.92	0.26	1.21	0.06	1	0.06	0.101
high	top	fast	1.34	1.30	0.90	3.5	1.63	0.71	0.45	0.01	1	0.01	0.038
				Total sum of data=		*17.8*			Sum=	**0.97**			
				Sum of squares of data=		15.91			Error=	**1.75**	16	0.11	
			Check:	**(1)**	**(2)**	**(3)**			S.S.total=	**2.72**			
			42	**85**	**170**	**340**							

Data Table for Analysis of Variance

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	f calc	Significant?
a=moisture	0.17	1	0.17	1.51	no
b=location	0.00	1	0.00	0.01	no
ab	0.04	1	0.04	0.36	no
c=fr.rate	0.29	1	0.29	2.63	no
ac	0.40	1	0.40	3.68	no
ac	0.06	1	0.06	0.56	no
abc	0.01	1	0.01	0.08	no
Error	1.75	16	0.11		

f 0.05 (1,16)=4.49
f 0.01 (1,16)=8.53

Appendix C-1. ANOVA Calculations for Freezing for Low Level Contaminated Clay Soil

INTRODUCTORY COMMENTS FOR APPENDIX C-1 and C-2.

- The data contained in these appendices are the analysis of variance (ANOVA) calculations to test the significance of freezing.

- The data is grouped according to PAH compound.

- For cases where variables were found to be insignificant, data were averaged. For example, location of contamination and moisture content were both found to be insignificant variables for naphthalene for sand. Therefore, data for the frozen samples taken from the top of the soil and from the bottom were averaged, data for the frozen soil for the low and high level of moisture content were averaged, and data for the slow and fast freezing rates were averaged. These averages appear in the "frozen avg." data row(s) in the ANOVA calculation tables.

- For cases where moisture content was significant, separate ANOVAs were calculated for the low and high level of moisture content. Again, though, the data from different locations were averaged because location was found to be insignificant for each PAH analyzed.

- The "Sums" column includes the sum of the "unfrozen" data and the "frozen" data.

- The calculated F value is compared to the tabulated F values to determine the level of significance of freezing.

ANOVA Data for Significance of Freezing- for CLAY Soil

TOTAL PAHs

Low moisture content: TOTAL PAHs

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Frozen avg	83.08	81.91	77.27	80.93	82.29	85.23	490.70	Freezing	13.89	1	13.89	1.0948	90%-3.29
Unfrozen	81.07	80.20	81.15	71.10	83.12	81.15	477.79	Error	126.87	10	12.69		95%-4.96
							968.49	Total	140.76	11			99%-10.04

High Moisture content: TOTAL PAHs

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	80.61	86.73	81.97	87.54	79.71	87.35	503.91	Freezing	187.51	1	187.51	4.8920	90%-3.29
Frozen avg	82.22	92.25	101.66	83.05	98.87	93.32	551.35	Error	383.29	10	38.33		95%-4.96
							1055.26	Total	570.80	11			99%-10.04

ACENAPHTHENE

Low moisture content: ACENAPHTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	23.28	20.71	24.96	21.80	20.93	24.96	136.64	Freezing	0.01	1	0.01	0.0025	90%-3.29
Frozen avg	25.81	21.75	21.54	21.86	23.57	21.82	136.33	Error	32.60	10	3.26		95%-4.96
							272.97	Total	32.61	11			99%-10.04

High Moisture content: ACENAPHTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	21.52	24.66	22.11	24.31	22.57	24.73	139.90	Freezing	22.10	1	22.10	9.9901	90%-3.29
Frozen avg	25.27	28.12	26.92	23.605	26.61	25.66	156.19	Error	22.12	10	2.21		95%-4.96
							296.09	Total	44.22	11			99%-10.04

ANOVA Data for Significance of Freezing- for CLAY Soil

FLUORENE

Low moisture content: FLUORENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	19.00	18.61	19.42	17.02	19.12	19.42	112.59	Freezing	0.66	1	0.66	0.9571	90%-3.29
Frozen avg	20.05	18.86	18.02	19.075	19.59	19.83	115.41	Error	6.90	10	0.69		95%-4.96
							228.00	Total	7.56	11			99%-10.04

High Moisture content: FLUORENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	18.65	20.67	18.79	20.61	19.49	21.27	119.48	Freezing	10.64	1	10.64	5.7591	90%-3.29
Frozen avg	20.76	21.99	23.31	19.31	23.51	21.92	130.78	Error	18.48	10	1.85		95%-4.96
							250.26	Total	29.12	11			99%-10.04

PHENANTHRENE

Low moisture content: PHENANTHRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	21.62	25.39	20.26	18.86	22.50	20.26	128.89	Freezing	15.09	1	15.09	2.8377	90%-3.29
Frozen avg	21.05	25.09	21.50	24.42	23.09	27.21	142.345	Error	53.16	10	5.32		95%-4.96
							271.235	Total	68.25	11			99%-10.04

High moisture content: PHENANTHRENE

	Replicate Data						Sums	Variation	Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	25.16	24.65	25.62	27.67	24.28	25.96	153.34	Freezing	12.91	1	12.91	1.7447	90%-3.29
Frozen avg	22.63	25.34	32.49	26.26	30.91	28.16	165.79	Error	73.97	10	7.40		95%-4.96
							319.13	Total	86.88	11			99%-10.04

ANOVA Data for Significance of Freezing- for CLAY Soil

FLUORANTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	13.21	9.97	7.29	10.04	12.84	7.29	123.92	Freezing	1.88	1	1.88	0.6674	90%-3.29
Unfrozen	10.91	11.92	10.60	10.75	8.45	10.65	130.64	Error	62.02	22	2.82		95%-4.96
Frozen avg	13.21	10.89	9.50	9.61	9.66	10.21	254.56	Total	63.91	23			99%-10.04
Frozen avg	9.45	11.07	13.41	10.00	11.65	12.00							

PYRENE

Low moisture content: PYRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	2.30	2.22	3.03	1.94	2.77	3.03	15.29	Freezing	0.00	1	0.00	0.0135	90%-3.29
Frozen avg	2.53	2.37	2.21	2.75	2.69	2.91	15.44	Error	1.39	10	0.14		95%-4.96
							30.73	Total	1.39	11			99%-10.04

High Moisture content: PYRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	2.32	2.83	2.68	2.94	2.55	3.41	16.73	Freezing	1.13	1	1.13	3.4619	90%-3.29
Frozen avg	2.34	3.85	3.66	2.67	3.90	4.00	20.41	Error	3.25	10	0.33		95%-4.96
							37.14	Total	4.38	11			99%-10.04

Appendix C-2. ANOVA Calculations for Freezing for Highly Contaminated Sand Soil

ANOVA Data for Significance of Freezing- for SAND Soil

TOTAL PAHs

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	55.50	51.37	61.18	57.63	39.83	61.96	611.71	Freezing	3.63	1	3.63	0.0615	90%-3.29
Unfrozen	35.47	53.05	55.49	54.29	48.50	46.78	621.05	Error	1300.95	22	59.13		95%-4.96
Frozen avg	36.12	51.14	50.68	56.18	62.00	56.33	1232.76	Total	1304.58	23			99%-10.04
Frozen avg	45.06	48.35	52.84	44.65	47.47	60.92							

NAPHTHALENE

Low moisture content: NAPHTHALENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	7.40	6.03	3.55	8.33	5.20	1.91	32.42	Freezing	0.00	1	0.00	0.0001	90%-3.29
Frozen avg	7.35	5.74	4.47	7.65	5.44	1.69	32.325	Error	52.24	10	5.22		95%-4.96
							64.745	Total	52.24	11			99%-10.04

High Moisture content: NAPHTHALENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	4.14	1.16	3.28	0.89	0.49	0.73	10.69	Freezing	0.06	1	0.06	0.0306	90%-3.29
Frozen avg	3.73	1.45	2.90	0.48	0.64	0.63	9.81	Error	21.10	10	2.11		95%-4.96
							20.50	Total	21.16	11			99%-10.04

ANOVA Data for Significance of Freezing- for SAND Soil

ACENAPHTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	7.90	7.33	8.53	7.73	6.57	9.28	95.35	Freezing	0.01	1	0.01	0.0092	90%-3.29
Unfrozen	6.72	7.84	8.95	8.73	7.92	7.85	94.92	Error	18.81	22	0.86		95%-4.96
Frozen avg	6.72	6.84	8.37	7.03	7.45	9.76	190.27	Total	18.82	23			99%-10.04
Frozen avg	6.41	8.53	8.34	8.86	8.27	8.36							

FLUORENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	6.60	6.07	7.20	6.73	5.63	7.59	78.46	Freezing	0.00	1	0.00	0.0055	90%-3.29
Unfrozen	5.33	6.64	7.39	6.85	6.13	6.30	78.21	Error	10.75	22	0.49		95%-4.96
Frozen avg	5.94	5.97	6.95	5.90	5.97	7.76	156.67	Total	10.76	23			99%-10.04
Frozen avg	5.22	6.78	6.82	6.96	7.20	6.75							

ANOVA Data for Significance of Freezing- for SAND Soil

FLUORANTHENE

Low moisture content: FLUORANTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	9.40	9.43	12.82	9.53	6.07	13.96	61.21	Freezing	5.04	1	5.04	0.6395	90%-3.29
Frozen avg	6.59	8.07	11.27	6.00	8.29	13.23	53.43	Error	78.88	10	7.89		95%-4.96
							114.64	Total	83.92	11			99%-10.04

High Moisture content: FLUORANTHENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	6.18	13.82	12.31	15.17	11.17	11.04	69.69	Freezing	1.01	1	1.01	0.1049	90%-3.29
Frozen avg	6.43	12.65	11.33	14.64	14.64	13.50	73.165	Error	95.92	10	9.59		95%-4.96
							142.855	Total	96.93	11			99%-10.04

PYRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	3.13	3.20	4.62	3.20	2.07	4.75	40.60	Freezing	0.01	1	0.01	0.0061	90%-3.29
Unfrozen	2.02	3.91	2.95	3.3	3.96	3.49	40.22	Error	21.68	22	0.99		95%-4.96
Frozen avg	2.22	3.20	4.10	2.00	2.75	5.66	80.82	Total	21.69	23			99%-10.04
Frozen avg	2.045	3.01	2.83	3.95	4.675	3.785							

ANOVA Data for Significance of Freezing- for SAND Soil

BENZO(b+k)PYRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	0.63	0.67	1.20	0.70	0.27	1.16	9.15	Freezing	0.00	1	0.00	0.0308	90%-3.29
Unfrozen	0.34	0.85	0.75	0.87	0.84	0.87	8.90	Error	1.94	22	0.09		95%-4.96
Frozen avg	0.44	0.70	0.90	0.30	0.44	1.18	18.045	Total	1.94	23			99%-10.04
Frozen avg	0.335	0.71	0.71	0.99	1.175	1.025							

PHENANTHRENE

SLOW Freezing Rate: PHENANTHRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	15.50	14.10	16.83	8.53	14.52	15.94	85.42	Freezing	3.75	1	3.75	0.6417	90%-3.29
Frozen avg	12.84	13.50	14.09	9.83	14.24	14.23	78.72	Error	58.39	10	5.84		95%-4.96
							164.14	Total	62.13	11			99%-10.04

FAST Freezing Rate: PHENANTHRENE

	Replicate Data						Sums	Source of Variation	Sum of Squares	D.F.	Mean Sq.	F	F crit
Unfrozen	16.43	11.20	17.05	15.36	12.85	11.46	84.35	Freezing	5.38	1	5.38	0.9756	90%-3.29
Frozen avg	12.70	13.45	15.61	15.63	18.62	16.39	92.385	Error	55.14	10	5.51		95%-4.96
							176.74	Total	60.52	11			99%-10.04

Appendix D-1. Raw Data for Grain Size Soil Analysis Test

SAND

Wet sieved soil Dec. 16 194. Left to dry over weekend.

SAND

UNIVERSITY of ALBERTA
DEP'T. of CIVIL ENGINEERING
SOIL MECHANICS LABORATORY
SIEVE ANALYSIS

PROJECT M. Sc. Thesis
SITE Cochrane
SAMPLE Extracted soil
LOCATION ⟶
HOLE DEPTH
TECHNICIAN AB DATE

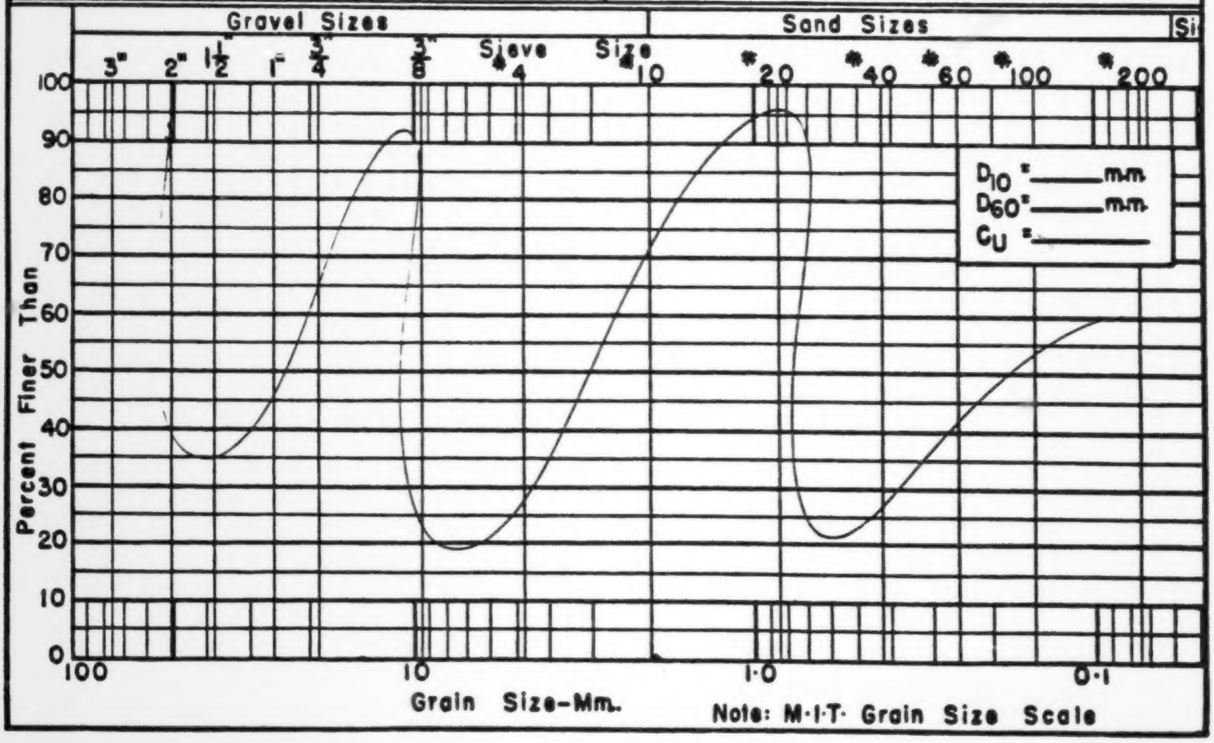
Total Dry Weight of Sample 320.509	Sieve No.	Size of Opening Inches	Size of Opening Mm.	Weight Retained gms.	Total Wt. Finer Than gms.	Percent Finer Than	% Finer Than Basis Orig. Sample
Initial Dry Weight							
Retained No. 4							
Tare No.______							
Wt. Dry + Tare______							
Tare______		3/4	19.10	?			
Wt. Dry______		3/8	9.52		320.50	100 %	
	4	.185	4.76	7.28	313.22	97.7%	
Passing	4						
Initial Dry Weight							
Passing No. 4	10	.079	2.000	26.02	287.20	89.6%	
Tare No.______	20	.0331	.840	84.53	202.67	63.2%	
Wt. Dry + Tare______	40	.0165	.420	85.47	117.20	36.6%	
Tare______	60	.0097	.250	50.40	66.80	20.8%	
Wt. Dry______	100	.0059	.149	27.38	39.42	12.3%	
	200	.0029	.074	16.48	22.94	7.2%	
~~Passing~~	~~200~~ 325		.045	5.40	17.54	5.5%	

Description of Sample______

Time of Sieving______

Method of Preparation Performed a wet sieve w/ #325. Then dried for 3 days in 105°C oven. Then performed analysis.

Remarks Losses not accounted for (soil stuck to tins when transferring, also stuck to sieves)



SAND

UNIVERSITY of ALBERTA
DEP'T. of CIVIL ENGINEERING
SOIL MECHANICS LABORATORY

SIEVE ANALYSIS

PROJECT
SITE
SAMPLE "CLEAN" SOIL
LOCATION
HOLE DEPTH
TECHNICIAN DATE

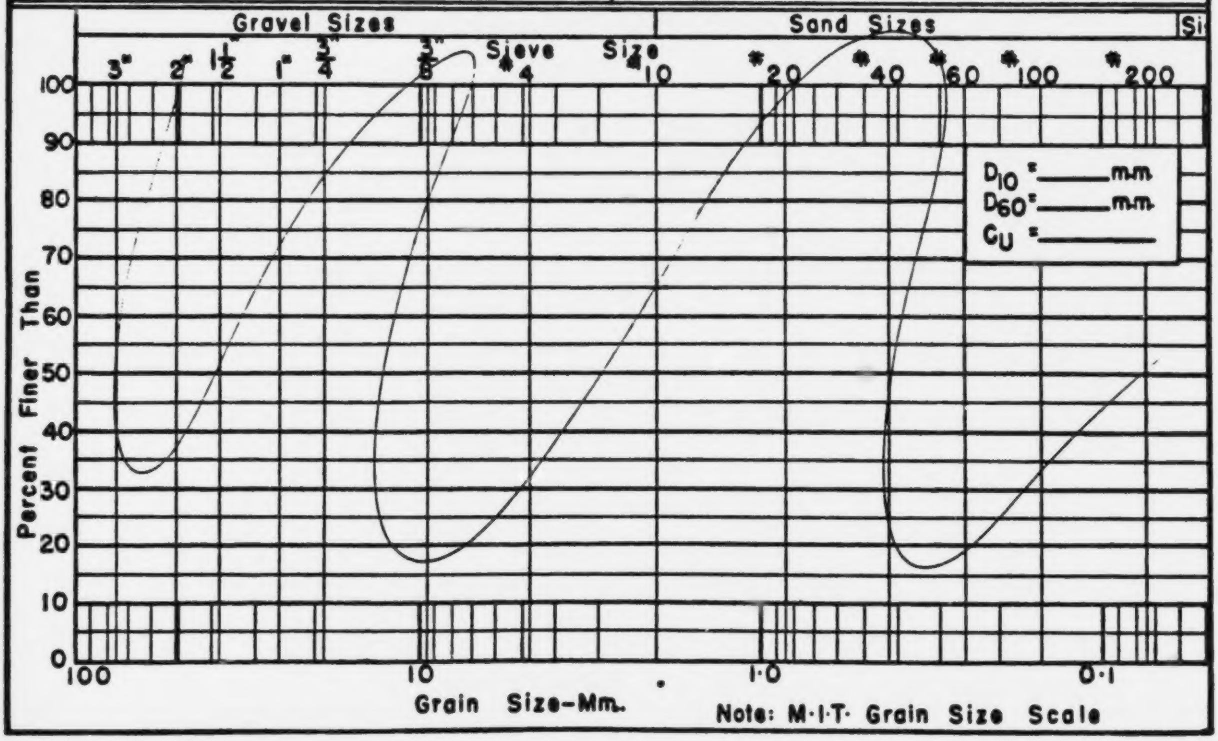
Total Dry Weight of Sample 357.84	Sieve No.	Size of Opening Inches	Size of Opening Mm.	Weight Retained gms.	Total Wt. Finer Than gms.	Percent Finer Than	% Finer Than Basis Orig. Sample
Initial Dry Weight Retained No. 4							
Tare No.							
Wt. Dry + Tare							
Tare		3/4	19.10		357.84		
Wt. Dry		3/8	9.52				
	4	.185	4.76	0			
Passing	4			0			
Initial Dry Weight				0 - 4			
Passing No. 4	10	.079	2.000	47.41	310.43	86.8	
Tare No.	20	.0331	.840	74.52	235.91	65.9	
Wt. Dry + Tare	40	.0165	.420	78.26	157.65	44.1	
Tare	60	.0097	.250	49.08	108.57	30.3	
Wt. Dry	100	.0059	.149	35.39	73.18	20.5	
	200	.0029	.074	50.93	22.25	6.2	
Passing	~~200~~ 325		.045	11.19	11.06	3.1 %	

Description of Sample

Time of Sieving

Method of Preparation none.

Remarks Losses not accounted for



CLAY

```
###########################################################################################
#   UNIVERSITY OF ALBERTA        #       PROJECT :         MSc.
#                                #       SAMPLE  :         Contaminated - Edmonton D.T.
#  DEP'T OF CIVIL ENGINEERING    #       HOLE    :                   DEPTH
#                                #       TECH    :         AB        DATE    March 13, 1995
#       HYDROMETER TEST (R.P.S)  #
###########################################################################################
#Hydrometer(151H)#:   11079      # note: Spread Sheet Developed For 151H Hydrometer
#Meniscus Corr.Cm.:  0.0005 <--use actual correction
#Dispersing Agent :Calgon                 Amount  :4%            125 ml.
#Dispersing Corr. :  0.0035
#S.G. of Soil     :    2.66 <<--
#Wt. of Dry Soil  :    52.3      grams                     Ph=?
#S.G. of Liquid   :    1.00
#
###########################################################################################
#          TIME                   TIME       ELAPSED   TEMP                       % FINER  DIAMETER  AVG TEMP VISCOSITY    TEMP
                               (hrs:min :sec)  TIME      C        R'h      Rh       THAN      mm         c      poise       Ct
  YEAR      MONTH      DAY     (00 : 00 : 00)  (min)
#
#1995           3         13   11 : 37 :  0      0.0                                -3071.3                0.0 0.0175173      0.54
#                         13   11 : 38 : 30      1.5      28.0    1.0265   1.0261      75.4    0.0363       14.0 0.0117975      2.60
#note: if month changes   13   11 : 39 :  0      2.0      28.0    1.0255   1.0251      72.4    0.0269       28.0 0.0083665      2.60
#you must adjust elapsed  13   11 : 41 :         4.0      27.5    1.0248   1.0242      69.6    0.0193       27.7 0.0084077      2.38
#time.                    13   11 : 45 :         8.0      27.0    1.0230   1.0222      63.4    0.0140       27.2 0.0084923      2.16
#                         13   11 : 53 :        16.0      27.0    1.0225   1.0217      61.8    0.0100       27.0 0.0085357      2.16
#                         13   12 :  9 :        32.0      26.5    1.0215   1.0205      58.1    0.0072       26.7 0.0085798      1.96
#                         13   12 : 41 :        64.0      26.0    1.0205   1.0193      54.4    0.0052       26.3 0.0086702      1.75
#                         13   15 : 41 :       244.0      24.2    1.0172   1.0153      42.3    0.0028       25.1 0.0088893      1.09
#                         14    8 :  0 :      1223.0      23.5    1.0100   1.0078      19.5    0.0014       23.8 0.0091449      0.85
#                         14    9 : 30 :      1313.0      23.5    1.0100   1.0078      19.5    0.0013       23.5 0.0092197      0.85
#                         14   11 : 56 :      1459.0      23.5    1.0098   1.0076      18.9    0.0013       23.5 0.0092197      0.85
#                         14   15 : 48 :      1691.0      24.0    1.0095   1.0075      18.5    0.0012       23.8 0.0091661      1.02
#                         15    7 : 58 :      2661.0      23.5    1.0092   1.0070      17.0    0.0009       23.8 0.0091661      0.85
```

CLAY

```
****************************************************************************************************
*    UNIVERSITY OF ALBERTA        *      PROJECT :        MSc.
*                                 *      SAMPLE  :        Uncontaminated - Edmonton D.T.
   DEP'T OF CIVIL ENGINEERING     *      HOLE    :                 DEPTH
*                                 *      TECH    :        AB       DATE    March 13, 1995
*       HYDROMETER TEST (R.P.S)   *
****************************************************************************************************
*Hydrometer(151H)#:   11079      * note: Spread Sheet Developed For 151H Hydrometer
*Meniscus Corr.Cm.:  0.0005 <--use actual correction
*Dispersing Agent :Calgon               Amount  :4%           125 ml.
*Dispersing Corr. :  0.0035
*S.G. of Soil     :    2.66 <<--
*Wt. of Dry Soil  :    61.3      grams                     Ph-?
*S.G. of Liquid   :    1.00
*
****************************************************************************************************
*           TIME                  TIME        ELAPSED   TEMP                     % FINER  DIAMETER  AVG TEMP VISCOSITY    TEMP
*                           (hrs:min :sec)  TIME       C        R'h       Rh      THAN      mm        c       poise      Ct
*  YEAR     MONTH     DAY   (00 : 00 : 00)  (min)
*
*1995            3      13  12 : 12 :  0      0.0                               -2620.3                0.0 0.0175173    0.54
*                       13  12 : 12 : 30      0.5     26.0    1.0310    1.0298     73.9   0.0595      13.0 0.0121301    1.75
*note: if month changes 13  12 : 13 :  0      1.0     26.0    1.0305    1.0293     72.6   0.0360      26.0 0.0087165    1.75
*you must adjust elapsed 13  12 : 14 :        2.0     25.5    1.0295    1.0281     69.5   0.0259      25.7 0.0087636    1.56
*time.                  13  12 : 16 :        4.0     25.5    1.0290    1.0276     68.2   0.0185      25.5 0.0088113    1.56
*                       13  12 : 20 :        8.0     25.0    1.0280    1.0264     65.1   0.0133      25.2 0.0088598    1.37
*                       13  12 : 28 :       16.0     25.0    1.0270    1.0254     62.5   0.0096      25.0 0.0089090    1.37
*                       13  12 : 44 :       32.0     25.0    1.0255    1.0239     58.5   0.0069      25.0 0.0089090    1.37
                        13  15 : 42 :      210.0     24.0    1.0205    1.0185     44.5   0.0029      24.5 0.0090097    1.02
*                       14   8 :  2 :     1190.0     23.5    1.0170    1.0148     34.9   0.0013      23.8 0.0091661    0.85
*                       14   9 : 30 :     1278.0     23.5    1.0165    1.0143     33.6   0.0013      23.5 0.0092197    0.85
*                       14  11 : 57 :     1425.0     24.0    1.0160    1.0140     32.7   0.0012      23.8 0.0091661    1.02
*                       14  15 : 50 :     1658.0     24.0    1.0158    1.0138     32.2   0.0011      24.0 0.0091132    1.02
*                       15   8 :  0 :     2628.0     23.5    1.0150    1.0128     29.7   0.0009      23.8 0.0091661    0.85
```

Appendix D-2. Grain Size Graphs

Figure D-2.A. Sandy Soil Classification Profile - Contaminated

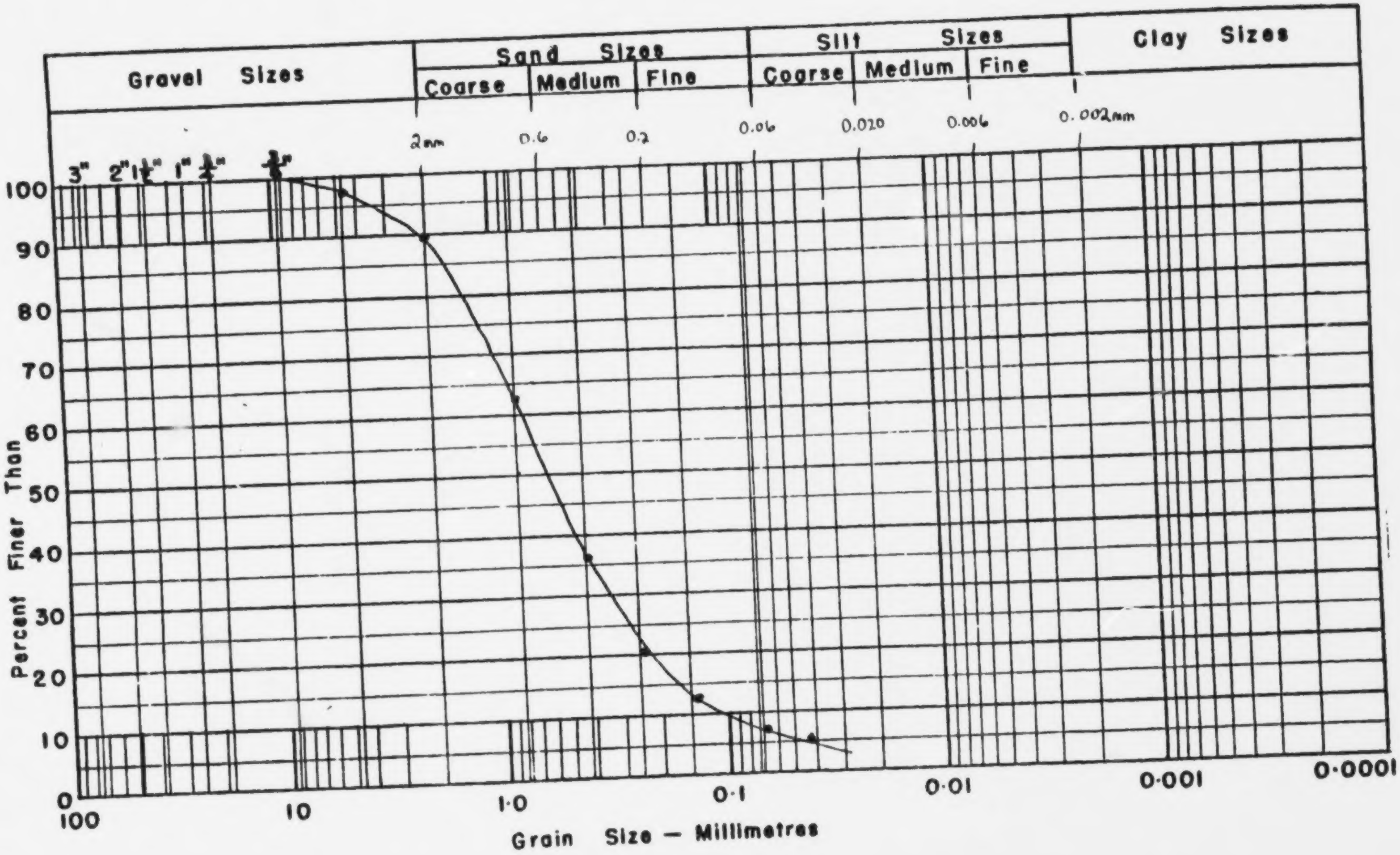


Figure D-2.B. Sandy Soil Classification Profile - Uncontaminated

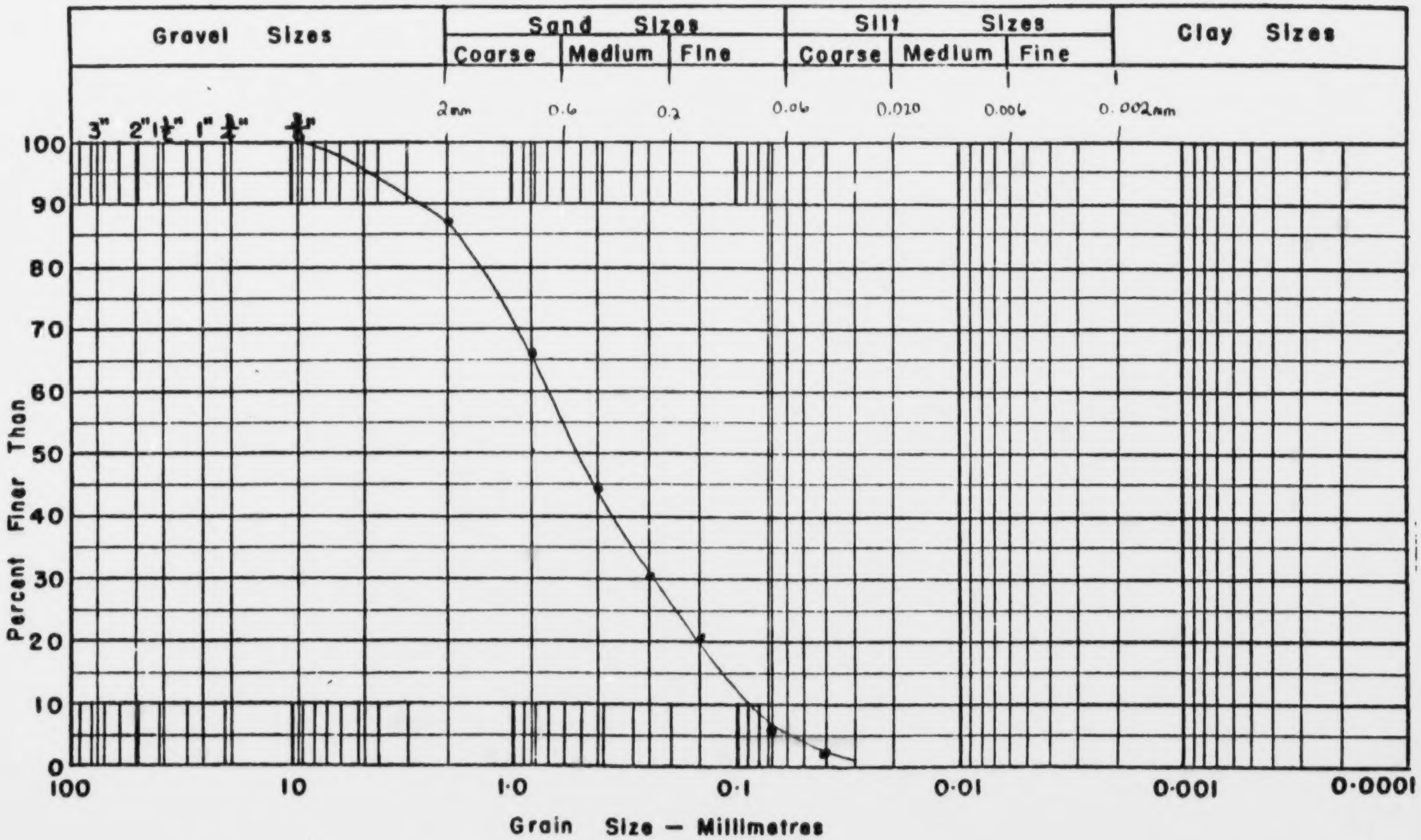
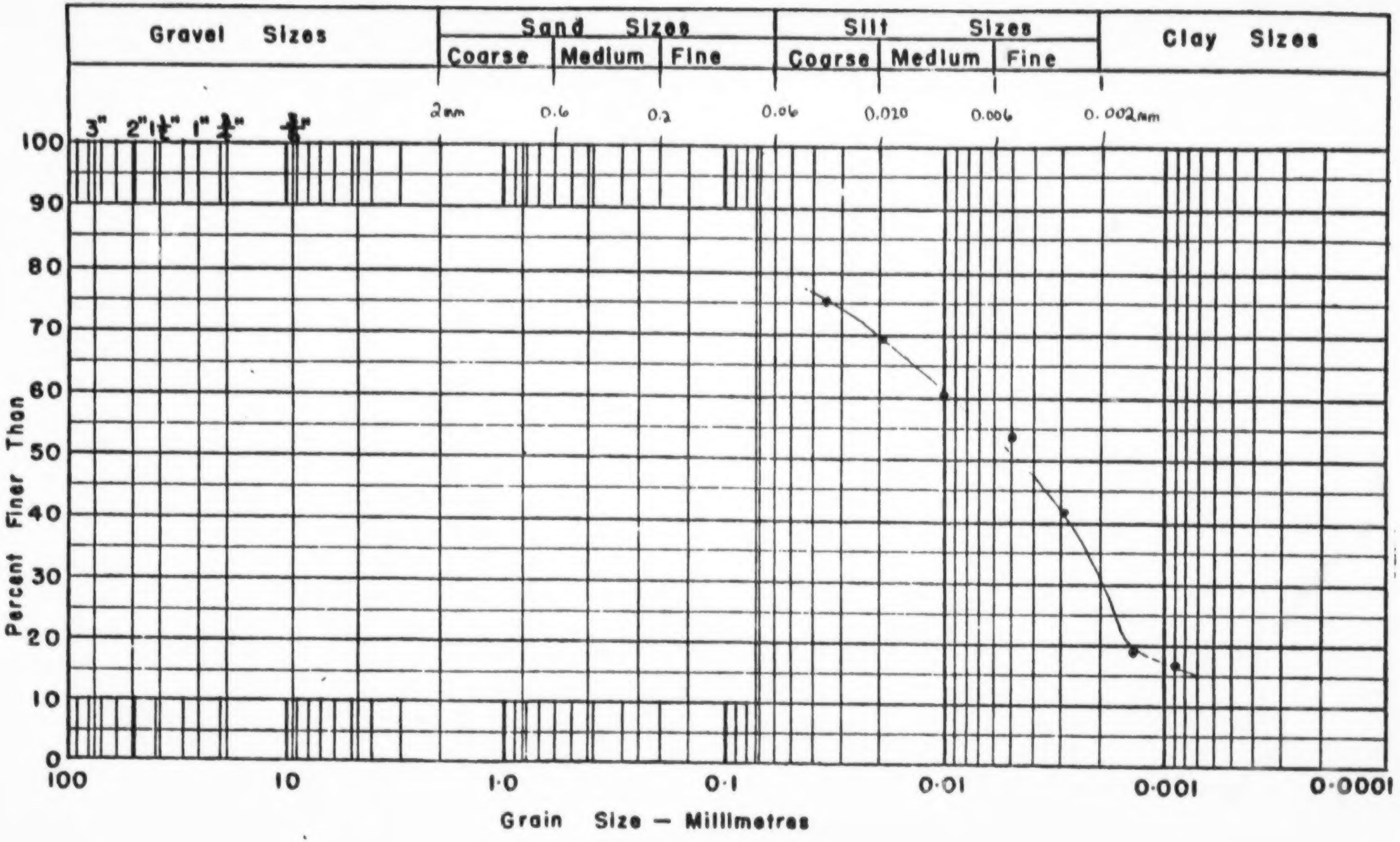


Figure D-2.C. Clay Soil Classification Profile - Contaminated



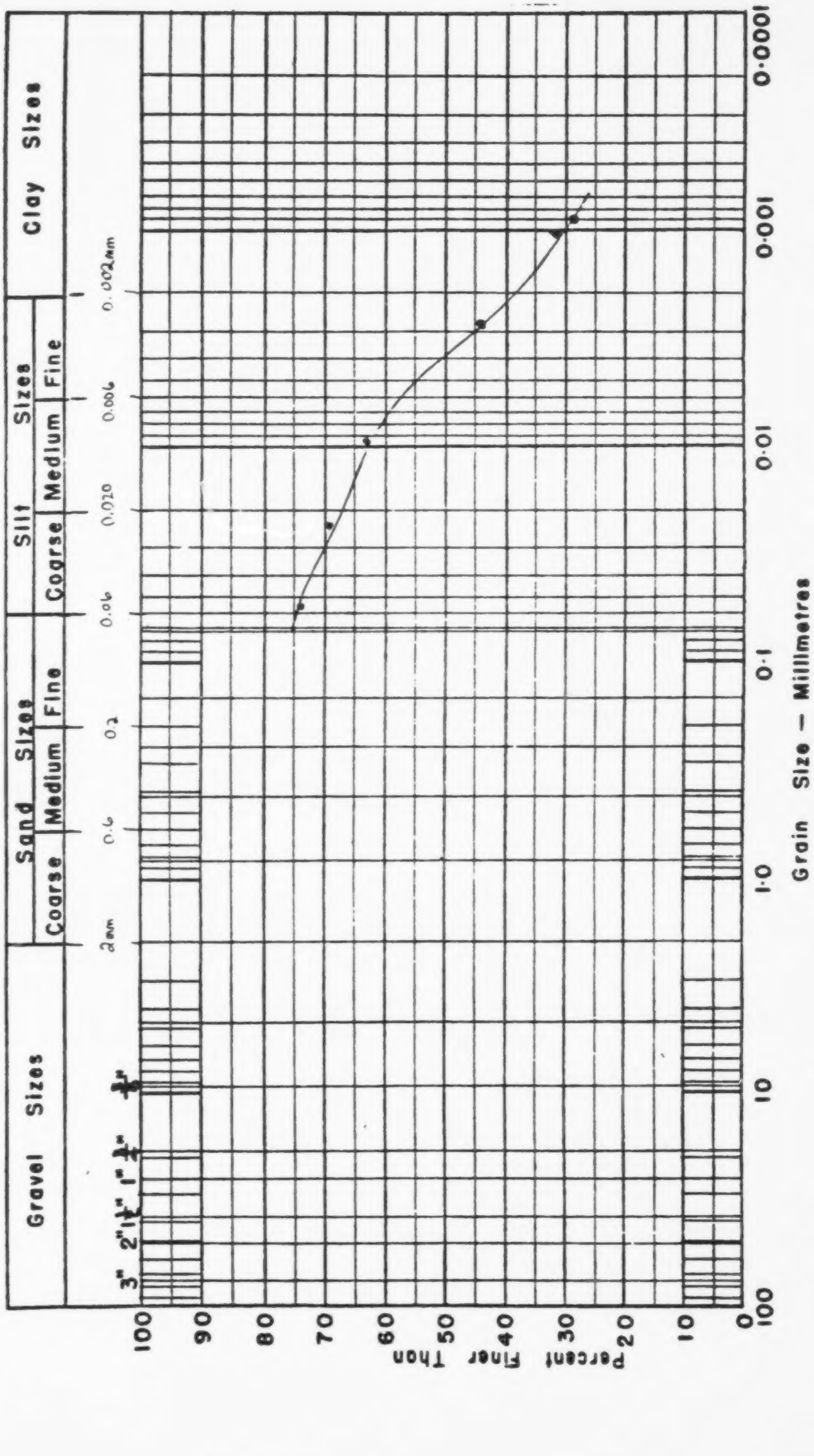


Figure D-2.D. Clay Soil Classification Profile - Uncontaminated

Appendix E-1. Table of Standard Deviations

INTRODUCTORY COMMENTS FOR APPENDIX E-1 and E-2.

- The data contained in this appendix are the an indication of precision between experimental runs with the same conditions.

- The data is grouped according to experimental conditions, listed at the top of each data set. Three sets of data are reported, the data for the unfrozen soil, data for the top of the frozen soil, and data for the bottom of the frozen soil.

- "Avgs." denotes the average aqueous phase PAH concentration for those runs listed.

- "Std. dev." is the standard deviation for the data for those runs.

- "Percent" is the coefficient of variation, the standard deviation divided by the mean expressed as a percentage.

- "Avg. error" is the average coefficient of variation for all the data for that set of experimental conditions, for the unfrozen, frozen top and bottom soil samples.

CLAY:Moisture content: low, Freezing Rate: slow

	Runs 1,9,17-UNFROZEN			Runs 1, 9, 17-TOP			Runs 1, 9, 17-BOTTOM			Avg.
	Avgs	Std.dev.	Percent	Avgs	Std.dev.	Percent	Avgs	Std.dev.	Percent	Error
Naphthalene	0.37	0.09	23.6	0.60	0.25	41.5	1.17	0.49	41.9	35.7
Acenaphthalene	0.58	0.22	38.7	0.54	0.08	15.7	0.57	0.11	19.8	24.7
Acenaphthene	22.41	2.05	9.1	22.33	2.05	9.2	23.73	3.41	14.4	10.9
Fluorene	18.90	0.55	2.9	18.04	0.99	5.5	19.89	1.85	9.3	5.9
Phenanthrene	23.04	2.45	10.6	21.59	1.85	8.6	23.50	3.16	13.4	10.9
Fluoranthene	10.98	2.39	21.7	11.00	1.47	13.4	11.40	2.53	22.2	19.1
Pyrene	2.37	0.39	16.6	2.28	0.15	6.5	2.46	0.28	11.4	11.5
Benz(a)anthracene	0.12	0.18	145.2	0.04	0.05	121.7	0.09	0.09	95.5	120.8
Chrysene	0.26	0.05	19.7	0.32	0.07	22.4	0.28	0.10	36.9	26.3
Benzo(b)pyrene	0.25	0.16	62.8	0.31	0.07	22.9	0.32	0.07	21.4	35.7
Benzo(k)pyrene	0.30	0.11	37.7	0.29	0.06	20.9	0.32	0.07	20.2	26.3
Benzo(a)pyrene	0.09	0.12	129.2	0.03	0.04	161.6	0.05	0.04	83.3	124.7

CLAY:Moisture content: low, Freezing Rate: fast

	Runs 2,10,18-UNFROZEN			Runs 2,10,18-TOP			Runs 2,10,18-BOTTOM			Avg.
	Avgs	Std.dev.	Percent	Avgs	Std.dev.	Percent	Avgs	Std.dev.	Percent	Error
Naphthalene	0.45	0.21	46.8	0.41	0.22	53.0	0.49	0.18	37.0	45.6
Acenaphthalene	0.56	0.23	41.7	0.61	0.08	13.8	0.64	0.06	9.9	21.8
Acenaphthene	21.88	1.92	8.8	22.38	1.31	5.8	22.44	1.59	7.1	7.2
Fluorene	18.26	1.21	6.6	19.01	1.05	5.5	19.99	0.58	2.9	5.0
Phenanthrene	20.62	2.84	13.8	23.84	2.73	11.5	25.97	2.53	9.7	11.6
Fluoranthene	10.85	3.43	31.6	9.54	0.97	10.2	10.11	1.09	10.8	17.5
Pyrene	2.45	0.57	23.4	2.59	0.25	9.8	2.97	0.29	9.8	14.3
Benz(a)anthracene	0.18	0.22	123.2	0.18	0.13	73.5	0.24	0.07	30.5	75.7
Chrysene	0.27	0.11	41.1	0.30	0.11	36.2	0.31	0.03	10.5	29.3
Benzo(b)pyrene	0.43	0.23	52.4	0.41	0.31	76.7	0.46	0.12	25.5	51.5
Benzo(k)pyrene	0.43	0.23	52.5	0.43	0.31	73.0	0.46	0.12	25.3	50.3
Benzo(a)pyrene	0.11	0.10	85.5	0.09	0.10	111.1	0.12	0.05	41.7	79.4

SAND:Moisture content: low, Freezing Rate: slow

	Runs 3,11,19-UNFROZEN			Runs 3,11,19-TOP			Runs 3,11,19-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	1.69	5.66	29.9	1.16	6.03	19.2	1.44	5.67	25.4	24.9
Acenaphthalene	0.07	0.24	29.7	0.05	0.21	22.9	0.14	0.17	84.9	45.8
Acenaphthene	0.57	7.92	7.2	0.88	7.24	12.2	1.88	7.37	25.6	15.0
Fluorene	0.59	6.62	8.9	0.74	6.13	12.0	1.69	6.43	26.3	15.7
Phenanthrene	1.64	15.48	10.6	1.78	13.44	13.2	1.79	13.29	13.5	12.5
Anthracene	0.78	2.61	29.8	0.69	2.04	33.7	0.94	2.29	41.2	34.9
Fluoranthene	2.05	10.55	19.5	1.09	7.96	13.7	4.44	9.32	47.6	26.9
Pyrene	0.83	3.65	22.8	0.41	2.91	14.1	1.73	3.43	50.5	29.1
Benz(a)anthracene	0.23	1.08	21.1	0.12	0.79	14.8	0.33	0.81	40.3	25.4
Chrysene	0.22	1.07	21.0	0.09	0.79	11.8	0.33	0.74	44.1	25.6
Benzo(b+k)pyrene	0.29	0.83	35.0	0.09	0.61	15.2	0.37	0.74	49.4	33.2
Benzo(a)pyrene	0.09	0.32	29.5	0.04	0.22	18.2	0.15	0.28	53.6	33.8

SAND: Moisture content: low, Freezing Rate: fast

	Runs 4,12,20-UNFROZEN			Runs 4,12,20-TOP			Runs 4,12,20-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	2.79	5.15	54.3	2.63	5.16	50.9	2.61	4.69	55.5	53.6
Acenaphthalene	0.07	0.21	36.0	0.05	0.23	20.5	0.07	0.20	34.4	30.3
Acenaphthene	1.43	7.86	18.2	1.52	8.25	18.4	1.34	7.92	16.9	17.8
Fluorene	1.57	6.65	23.6	1.38	6.60	20.9	0.94	6.48	14.6	19.7
Phenanthrene	5.77	14.90	38.7	2.81	14.19	19.8	1.72	13.65	12.6	23.7
Anthracene	1.06	2.22	47.9	0.65	1.93	33.6	0.55	1.89	29.4	37.0
Fluoranthene	5.90	9.85	59.9	4.32	9.31	46.4	3.00	9.02	33.3	46.5
Pyrene	1.71	3.34	51.2	2.05	3.50	58.5	1.64	3.44	47.8	52.5
Benz(a)anthracene	0.64	1.00	63.9	0.57	0.94	60.7	0.42	0.92	45.4	56.6
Chrysene	0.59	0.90	66.1	0.46	0.87	52.5	0.20	0.76	26.6	48.4
Benzo(b+k)pyrene	0.59	0.71	83.3	0.50	0.64	78.8	0.39	0.64	60.8	74.3
Benzo(a)pyrene	0.16	0.23	69.4	0.12	0.22	54.2	0.10	0.22	46.0	56.5

CLAY: Moisture content: high, Freezing Rate: slow

	Runs 5,13,21-UNFROZEN			Runs 5,13,21-TOP			Runs 5,13,21-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	0.28	0.34	82.0	0.04	0.26	15.3	0.08	0.32	23.8	40.4
Acenaphthalene	0.05	0.54	9.5	0.08	0.66	12.8	0.10	0.66	14.9	12.4
Acenaphthene	1.76	22.77	7.7	1.85	27.26	6.8	1.84	26.46	6.9	7.1
Fluorene	1.31	19.37	6.8	1.87	22.63	8.2	1.15	21.54	5.3	6.8
Phenanthrene	1.20	25.14	4.8	5.90	27.70	21.3	3.86	26.39	14.6	13.6
Fluoranthene	0.97	11.14	8.7	2.74	11.80	23.2	1.90	10.99	17.2	16.4
Pyrene	0.32	2.61	12.4	0.92	3.35	27.6	0.89	3.32	26.7	22.2
Benz(a)anthracene	0.02	0.06	41.5	0.02	0.02	137.2	0.04	0.02	210.2	129.7
Chrysene	0.13	0.27	48.0	0.14	0.30	45.9	0.17	0.38	46.2	46.7
Benzo(b)pyrene	0.20	0.40	50.5	0.10	0.37	28.1	0.19	0.31	59.6	46.1
Benzo(k)pyrene	0.20	0.40	50.0	0.15	0.30	51.4	0.13	0.34	37.4	46.3
Benzo(a)pyrene	0.07	0.06	125.6	nd	nd		nd	nd		

CLAY: Moisture content: high, Freezing Rate: fast

	Runs 6,14,22-UNFROZEN			Runs 6,14,22-TOP			Runs 6,14,22-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	0.11	0.23	49.0	0.04	0.28	13.7	0.13	0.32	42.4	35.0
Acenaphthalene	0.17	0.80	21.3	0.22	0.85	25.7	0.21	0.82	25.4	24.1
Acenaphthene	1.17	23.87	4.9	1.77	26.01	6.8	2.13	24.57	8.7	6.8
Fluorene	0.95	20.46	4.7	2.40	22.18	10.8	2.06	20.97	9.8	8.4
Phenanthrene	1.96	25.97	7.5	3.10	29.54	10.5	2.63	27.35	9.6	9.2
Fluoranthene	1.48	9.95	14.9	1.71	11.45	14.9	1.52	10.99	13.8	14.6
Pyrene	0.52	2.97	17.6	0.83	3.59	23.0	0.70	3.46	20.3	20.3
Benz(a)anthracene	0.10	0.05	215.6	0.00	0.00	0.0	0.00	0.00	0.0	71.9
Chrysene	0.11	0.18	64.1	0.16	0.17	98.3	0.07	0.28	24.5	62.3
Benzo(b)pyrene	0.13	0.11	115.5	0.08	0.32	26.1	0.09	0.32	28.4	56.7
Benzo(k)pyrene	0.04	0.23	16.5	0.08	0.31	25.0	0.09	0.31	29.9	23.8

SAND: Moisture content: high, Freezing Rate: slow

	Runs 7,15,23-UNFROZEN			Runs 7,15,23-TOP			Runs 7,15,23-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	1.33	2.86	46.6	1.09	2.67	41.0	0.92	2.71	34.0	40.5
Acenaphthalene	0.03	0.20	14.2	0.03	0.19	13.7	0.04	0.20	19.7	15.9
Acenaphthene	1.01	7.84	12.9	0.89	7.79	11.5	1.34	7.73	17.3	13.9
Fluorene	0.94	6.45	14.6	0.71	6.32	11.3	1.08	6.23	17.4	14.4
Phenanthrene	3.55	12.99	27.3	2.19	13.03	16.8	2.74	12.50	21.9	22.0
Anthracene	0.69	1.94	35.3	0.59	1.86	31.6	0.67	1.78	37.8	34.9
Fluoranthene	3.74	10.77	34.7	2.82	10.18	27.7	3.37	10.08	33.4	31.9
Pyrene	0.86	2.96	29.2	0.53	2.67	0.0	0.58	2.58	0.0	9.7
Benz(a)anthracene	0.24	0.64	37.3	0.13	0.48	26.8	0.14	0.44	31.0	31.7
Chrysene	0.19	0.55	34.4	0.18	0.49	35.9	0.25	0.48	51.9	40.7
Benzo(b+k)pyrene	0.25	0.64	38.7	0.18	0.56	31.3	0.25	0.60	40.9	36.9
Benzo(a)pyrene	0.06	0.13	44.3	0.06	0.15	41.2	0.06	0.15	44.4	43.3

SAND: Moisture content: high, Freezing Rate: fast

	Runs 8,16,24-UNFROZEN			Runs 8,16,24-TOP			Runs 8,16,24-BOTTOM			Avg.
	Std.dev	Average	Percent	Std.dev	Average	Percent	Std.dev	Average	Percent	Error
Naphthalene	0.38	0.70	53.7	0.10	0.61	16.0	0.09	0.56	16.7	28.8
Acenaphthalene	0.02	0.23	7.6	0.03	0.25	11.4	0.03	0.23	14.1	11.0
Acenaphthene	0.47	8.16	5.8	0.85	8.95	9.4	0.72	8.04	9.0	8.1
Fluorene	0.42	6.43	6.5	0.67	7.40	9.1	0.89	6.54	13.6	9.7
Phenanthrene	2.01	13.23	15.2	1.72	17.99	9.6	3.27	15.76	20.8	15.2
Anthracene	0.97	2.31	41.9	1.20	3.03	39.8	0.64	2.96	21.6	34.4
Fluoranthene	2.47	12.46	19.8	3.56	15.86	22.4	3.08	12.66	24.3	22.2
Pyrene	0.43	3.58	12.0	0.75	4.29	0.0	0.82	3.98	0.0	4.0
Benz(a)anthracene	0.35	0.86	41.1	0.30	1.19	24.9	0.33	1.24	26.5	30.8
Chrysene	0.21	0.68	30.2	0.29	0.92	31.0	0.32	0.78	41.3	34.2
Benzo(b+k)pyrene	0.09	0.86	10.5	0.25	1.18	20.8	0.27	0.95	28.1	19.8
Benzo(a)pyrene	0.06	0.22	25.8	0.18	0.31	57.6	0.07	0.29	24.2	35.9

Appendix F-1. Sand Soxhlet Data

Soxhlet extraction data for SAND

PAH compound	Low moisture content					High moisture content					
	Test 1	Test 2	Test 3	Test 4	Average	Test 1	Test 2	Test 3	Test 4	Test 5	Average
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Naphthalene	11.5	10.9	10.3	0.0	8.2	30.1	0.0	0.0	17.9	26.1	14.8
Acenaphthalene	23.7	20.9	23.8	28.6	24.2	26.2	35.8	32.5	40.5	23.3	31.7
Acenaphthene	1177.0	931.9	1126.0	1209.3	1111.0	1399.0	1226.8	1104.9	1264.6	1153.0	1229.7
Fluorene	1081.4	706.8	977.5	1302.3	1017.0	1774.7	4279.9	3841.7	4589.3	1425.5	3182.2
Phenanthrene	2328.7	1486.5	2034.4	5351.8	2800.4	4401.3	4200.8	3782.8	4163.0	3645.6	4038.7
Anthracene	944.7	960.6	853.4	1557.3	1079.0	1701.4	1576.5	1442.0	1645.7	1203.1	1513.7
Fluoranthene	4344.0	4937.6	6027.2	5827.5	5284.1	2950.6	6115.7	5293.7	2750.1	3106.0	4043.2
Pyrene	1469.9	1232.4	1479.9	1936.2	1529.6	1638.1	1604.9	1405.9	1472.2	1497.2	1523.7
Benz(a)anthracnen	481.5	441.1	478.0	692.2	523.2	477.7	505.3	405.5	493.2	485.1	473.4
Chrysene	182.1	150.9	249.8	317.8	225.1	376.1	232.4	212.9	224.4	323.3	273.8
Benzo(b+k)pyrene	668.8	577.6	646.1	754.7	661.8	683.0	698.7	708.4	603.7	630.2	664.8
Benzo(a)pyrene	99.8	116.0	106.9	149.8	118.1	138.3	164.1	89.3	118.6	122.6	126.6
Indeno(1,2,3-c,d)pyrene	34.5	33.0	34.6	45.2	36.8	29.6	37.5	31.5	27.5	32.7	31.7
Dibenz(a,h)anthracene	13.3	12.7	13.0	20.4	14.8	11.4	14.3	12.4	11.6	12.5	12.4
Benzo(g,h,i)perylene	25.6	29.4	27.5	41.8	31.1	34.4	39.3	34.2	30.4	35.5	34.8
TOTALS	12886.4	11648.0	14088.2	19234.9	14464.4	15671.9	20731.9	18397.7	17452.6	13721.5	17195.1

Note: Units are µg/g of PAHs per gram of dry soil

Appendix F-2. Clay Soxhlet Data

Data for Soxhlet Extractions for Clay Soil

	Low Moisture Content									
PAH Compound	Sox1a+b average	Sox2a+b average	Sox9a+b average	Sox 17	Sox9a+b & 17 avg.	Soxh10	Soxh10	Sox 18	Sox 10a+b & 18 avg.	**Grand average**
Naphthalene	5.65	3.86	10.04	2.94	6.49	6.17	5.72	5.16	5.68	**5.42**
Acenaphthalene	2.15	2.20	1.29	2.21	1.75	2.70	2.09	2.85	2.55	**2.16**
Acenaphthene	133.26	124.80	146.83	145.26	146.04	143.94	160.31	170.19	158.15	**140.56**
Fluorene	217.89	233.11	477.09	248.07	362.58	262.53	259.37	267.83	263.24	**269.20**
Phenanthrene	390.29	431.11	404.82	372.70	388.76	484.85	465.38	450.21	466.81	**419.24**
Anthracene	5.54	0.00	0.00	0.00	0.00	0.00	0.00	93.35	31.12	**9.16**
Fluoranthene	782.99	872.96	1314.54	1317.36	1315.95	877.75	1179.64	592.87	883.42	**963.83**
Pyrene	138.87	143.50	186.89	171.25	179.07	173.41	196.54	185.44	185.13	**161.64**
Benz(a)anthracene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	nd	0.00	**0.00**
Chrysene	43.45	29.65	30.09	22.21	26.15	53.28	26.76	54.72	44.92	**36.04**
Benzo(b)pyrene	47.38	59.12	61.48	51.81	56.65	48.11	51.51	56.15	51.92	**53.77**
Benzo(k)pyrene	51.29	65.47	45.58	61.96	53.77	54.44	58.62	64.28	59.11	**57.41**
Benzo(a)pyrene	5.49	7.66	0.00	1.73	0.87	5.65	3.72	5.07	4.81	**4.71**
TOTALS	1824.23	1973.41	2678.63	2397.50	2538.06	2112.83	2409.66	1948.12	2156.87	**2123.14**

Please note: all units are μg/g of PAHs per gram of dry soil.

Data for Soxhlet Extractions for Clay Soil

PAH Compound	High Moisture Content						
	Sox 5a+b	Sox 13	Sox 21	Sox 6	Sox 14	Sox22a+b	**Grand average**
Naphthalene	nd	4.27	4.06	5.61	7.7	5.18	**5.36**
Acenaphthalene	1.95	2.29	2.07	2.85	2.52	1.97	**2.27**
Acenaphthene	120.79	144.26	127.94	140.06	151.33	146.39	**138.46**
Fluorene	222.99	215.07	195.65	182.39	214.79	207.02	**206.32**
Phenanthrene	346.41	392.13	378.45	369.26	471.22	352.33	**384.97**
Anthracene	0.00	38.22	nd	48.13	0	30.50	**23.37**
Fluoranthene	1393.89	687.03	631.40	496.71	709.4	521.29	**739.95**
Pyrene	160.39	198.65	176.94	168.12	209.14	116.72	**171.66**
Benz(a)anthracene	0.00	3.67	nd	3.72	nd	2.70	**2.52**
Chrysene	19.46	13.68	16.41	17.15	59.15	18.01	**23.98**
Benzo(b)pyrene	58.66	60.50	55.99	55.15	64.8	38.73	**55.64**
Benzo(k)pyrene	71.75	63.76	60.08	56.87	74.83	30.42	**59.62**
Benzo(a)pyrene	0.28	5.54	4.71	3.96	5.15	5.94	**4.26**
TOTALS	2396.54	1829.07	1653.70	1549.98	1970.03	1477.16	**1812.75**

Please note: all units are µg/g of PAHs per gram of dry soil.